PRIMARY PRODUCTION AND NUTRIENT DYNAMICS OF THE SOUTHEASTERN BERING SEA SHELF

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April 20, 2004

Date

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THESIS

Presented to the Faculty
of the University of Alaska

in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

By
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Fairbanks, Alaska
May 2004

Abstract

Understanding the relationships between the distributions of organisms and oceanographic conditions was one of the major goals of the Southeastern Bering Sea Carrying Capacity (SEBSCC) study. As a part of SEBSCC, this study focused on the response of nutrients and primary production to the variations of physical conditions, the general distribution of primary production, and the dynamics of phytoplankton growth, and nutrient utilization over the middle shelf and shelf break regions. The concentration of nutrients and primary productivity were measured over the shelf during 1997-1999. Shipboard nutrient and iron addition experiments were conducted over the middle shelf and shelf break region of the southeastern Bering Sea shelf during 2000-2001.

The variations in physical conditions strongly affected the distribution of nutrients in the surface euphotic layer as well as in the deep layer. The offshore transport of the middle shelf water at mid-depth over the outer shelf may play a very important role in the export of materials, including regenerated iron, from the middle shelf to the shelf break. There were large seasonal and spatial variations in the development of the spring phytoplankton bloom due to the strength of upwelling and the slope of the front at the shelf break. However, annual primary production, estimated by combining carbon uptake data of the PROBES study and this study, were similar over the inner (133 g C m^{-2} y^{-1}), middle (144 g C m^{-2} y^{-1}) and outer (138 g C m^{-2} y^{-1}) shelves and the shelf break (143 g C m^{-2} y^{-1}). Nutrient addition studies showed that nitrogen availability was essential to continuous phytoplankton growth during summer, and that the interaction between ammonium and nitrate may play an important role in the dynamics of nutrient utilization.

The iron addition study suggested that lack of iron did not affect the growth of phytoplankton over the middle shelf, but slightly suppressed growth at the outside edge of the shelf break region.

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Acknowledgments

My great thanks to God, who began a good work in me and will carry it on to completion, for his guidance and protection of my family and myself in the process of doing the research and writing the dissertation. I would like to thank my family, Kyung Sook, Si Young, Ji Hyun, for their emotional support and patience. I'm really sorry that I was sometime not available for their most important moments of life. Without them, I could not have completed my research and dissertation. I would like to thank my parents and parents-in-law for their emotional and financial support. I also would like to thank my brother and sisters-in-law for their filling for my absence.

I would like to express my gratitude to my graduate committee members, Thomas Weingartner, Rolf Gradinger, and Richard Dugdale, for their time spent on my questions and for their valuable comments on this dissertation. I'm especially grateful to Susan Henrichs for her comments and invaluable time to work with my dissertation. I owe special thanks to Terry Whitledge, as my major graduate study advisor, for his comfortable personality, financial support, academic encouragement, and especially, because he opened his office door any time even with very trivial questions.

The financial support came from 1) the NOAA-funded Southeastern Bering Sea Carrying Capacity (SEBSCC) ecosystem project through the NOAA-UAF Cooperative Institute For Arctic Research (CIFAR) funded primary productivity study, 2) the NSF-funded Inner Shelf Front (InFront) study, and 3) the Summer Phytoplankton Processes and the Influence of Mesoscale Eddies on Shelf-Slope Exchange projects, both of which were funded under the North Pacific Marine Research Program.

Chapter 1. General Introduction

1.1. Importance of the Bering Sea

The Bering Sea is located in the sub-arctic region and consists of a deep ocean basin and wind, shallow shelf region (Scholl *et al.* 1968). It is connected to the North Pacific and the Arctic Ocean by passes along the Aleutian Island Chain and by the shallow and narrow Bering Strait, respectively (Fig.1.1). The water masses that enter the Bering Sea through the passes along the Aleutian Chain are very important to water properties and nutrient supplies for the southeastern Bering Sea shelf (Schumacher and Reed 1992; Stabeno *et al.* 2002). The water masses in the Bering Sea exhibit large biogeochemical variations over the shelf and the slope regions, which are closely related to large-scale variations of climate conditions (Coachman 1986; Sambrotto *et al.* 1986; Whitledge *et al.* 1986).

Strong currents comprised of three different water masses, including the Alaskan Coastal Water, Anadyr Water, and Bering Shelf Water, flow northward from the Bering Sea into the Chukchi Sea (Coachman *et al.* 1975; Coachman 1993). Alaskan Coastal Water is located on the east side of Bering Strait and originates along the coast in the southeastern Bering Sea. Anadyr Water is located on the west side of Bering Strait and is driven by a sub-surface flow over the shelf break at about 100-200m depth; it contains high nutrient concentrations. Bering Shelf Water is located between Alaskan Coastal Water and Anadyr Water and originates from the middle shelf of the Bering Sea. Thus, the large variations of water properties in the Bering Sea can be transferred to the western

Arctic Ocean through Bering Strait, and may change the biogeochemical cycles and the dynamics of the food webs. High rates of primary production (12-16 g C m^{-2} day^{-1}) have been measured in the Chirikov Basin and Chukchi Sea (McRoy *et al.* 1987). The high production primarily results from large, chain-forming diatoms, which are the main spring phytoplankton bloom species in the Bering Sea (Springer and McRoy 1993). This high production supports a benthic food web, which is later consumed by gray whales and walrus (Frost and Lowry 1981; Fay 1982; Grebmeier *et al.* 1988; Grebmeier *et al.* 1989).

The Bering Sea is very important, not only due to its connections with both the North Pacific and the Arctic Oceans, but also due to its unique biological, chemical and physical processes. In particular, it is one of the world's most productive regions, supporting abundant higher trophic level organisms such as fish, shellfish, sea birds, and marine mammals. Over the last few decades, the Bering Sea ecosystem has experienced tremendous changes, such as dramatic declines in the abundance of several species of marine mammals and sea birds, which has been of great concern to fishermen, the research community, and the management agencies. However, it is still uncertain whether the declines resulted from over-fishing or from variations in environmental conditions (NRC 1996). It has been suggested that a change in the dynamics of the food web, due to variations of climate, is one explanation for the fluctuations observed in this ecosystem (Springer 1998).

1.2. Previous research programs

Many research studies have been conducted in the Bering Sea. The Outer Continental Shelf Environmental Assessment Program (OCSEAP) provided detailed hydrographic data during the 1960s and 1970s, which played a very important role in the development of Processes and Resources of the Bering Sea (PROBES), an interdisciplinary study that was conducted in the southeastern Bering Sea shelf region from the late 1970s to the early 1980s. The PROBES study, which focused on understanding the ability of the Bering Sea to support the higher trophic levels of crab, fish, birds, and mammals, provided extremely valuable knowledge of physical, chemical, and biological conditions and their relationship to the higher trophic levels (Coachman 1986; McRoy *et al.* 1986; Sambrotto *et al.* 1986; Smith and Vidal 1986; Walsh and McRoy 1986; Whitledge *et al.* 1986). In contrast to the PROBES study, Inner Shelf Transfer and Recycling (ISHTAR) was conducted in the northern Bering Sea. ISHTAR was designed to study the fate of the dissolved and particulate phases of carbon, nitrogen, phosphorus, and silicon in the northern Bering and southern Chukchi Seas (Walsh *et al.* 1989).

Recently, two major studies have been conducted over the southeastern Bering Sea shelf. One was the Southeastern Bering Sea Carrying Capacity (SEBSCC) program and the other was the Inner Front (InFront) study. The former focused on four central issues: (1) the influence of climate variability, (2) limiting factors for population growth, (3) the relationship between biological distributions and oceanographic conditions, and (4) controlling factors governing the primary and secondary production over the

southeastern Bering Sea shelf. The latter program studied high summer production along the structural front between the well-mixed waters of the coastal domain and the two-layer system of the middle domain (Macklin *et al.* 2002).

1.3. Southeastern Bering Sea shelf

1.3.1. Physical setting

The southeastern Bering Sea is a shallow and broad continental shelf, which extends over 500 km from the coast to the shelf break, even in the narrowest section (Coachman 1986). The sea bottom is a generally flat and featureless plain with a mean bottom slope of less than 0.2×10^{-3}, but two regions of steep bottom gradient occur along the 50m and 100m isobaths, which divide the southeastern Bering Sea shelf into three depth domains: coastal (0<H<50m), central (50<H<100m), and outer [100<H<150 (shelf break)]. These depth domains overlap with the three hydrographic domains, which are separated by frontal systems. The inner and middle fronts, which are centered along the 50m and 100m isobaths, are closely related to the steep bottom slope at those depths. The shelf break front, located along the ~170m isobath, separates the outer shelf domain from the open ocean (Askren 1972; Coachman 1986). The frontal systems reflect unique hydrographic, biological, and chemical characteristics within each domain (Coachman 1986). The inner shelf extends from the coast to the 50m isobath and has a homogeneous water column due to the overlapping of tidal and wind mixing energy within the shallow depth range of the water column. The middle shelf is located between 50m and 100m depth, where the water column is deep enough to separate the wind-driven surface mixed layer from the tidally driven bottom mixed layer, resulting in a two-layered system during

summer. The outer shelf is located at depth between 100m and 170m and has three layers, with a uniform density in the surface and bottom layers, which are separated by a middle layer with fine structures reflecting mixing processes (Coachman 1986).

1.3.2. Currents

The general pattern of circulation in the southeastern Bering Sea shelf is cyclonic, driven by sub-tidal flows due to non-linear interactions between the dominant tidal currents and bottom topography (Schumacher and Stabeno 1998; Kowalik 1999). In the inner shelf, a significant northward mean flow (1-6 cm s^{-1}) is centered along the 50m isobath, originating from the Alaska Coastal Current, which enters the Bering Sea through Unimak Pass and is reinforced by the addition of fresh water (Reed 1995; Schumacher and Stabeno 1998). Over the middle shelf, mean flow is weak. However, there are short duration, large fluctuations in strong subtidal currents, which may result in fluxes onto the middle shelf (Schumacher and Stabeno 1998). There is a weak cross-shelf weak flow north of the Pribilof Islands, which transports nutrient rich slope water into the inner shelf regions (Stabeno *et al.* 2001). Over the outer shelf, there is a northward mean flow (4-8 cm s^{-1}) along the 100m isobath, which originates from the flow that enters the Bering Sea through Unimak Pass. In addition, there is a strong northward flow (> 10 cm s^{-1}) at the inshore edge of the Bering Slope Current over the shelf break (Schumacher and Stabeno 1998). There is also a cross-shelf component of mean flow (1-5 cm s^{-1}), short duration current pulses (20-30 cm s^{-1}).

1.3.3. Sea ice

The southeastern Bering Sea shelf is relatively shallow, and a large proportion of the shelf region experiences a seasonal advance and retreat of sea ice. During the last three decades, there have been large variations in the spatial distributions of sea ice over the southeastern Bering Sea shelf (Niebauer 1988). The dynamics of sea ice over the shelf are closely related to the movement of the Aleutian Low along the Aleutian Island chain. The variations of the location and strength of the Aleutian Low are related to the El Nino-Southern Oscillation (ENSO) and the Pacific Decadal Oscillation (PDO) in the southeastern Bering Sea. However, neither ENSO nor PDO can explain all of the fluctuations of sea ice. Ice-edge algal blooms occur along the margin of retreating sea ice, which contribute up to 65% of annual production over the middle shelf of the southeastern Bering Sea. A large amount of the primary production of ice-edge blooms escapes pelagic grazing and is available to the benthic community due to the cold water temperatures, which delay maturation of copepods. The situation may differ during warm years, when pelagic grazing can be greater (Coyle and Pinchuk 2002).

The variations in sea ice dynamics have a profound impact on the ecosystem. For example, the sea ice influences the production and distribution of cold bottom water, which in turn determines water column temperatures that control the distribution of favorable habitat for subarctic fish species in this region (Wyllie-Echeverria and Ohtani 1999). Also the abundance of spring zooplankton shows temperature dependency over the middle domain of the southeastern Bering Sea shelf (Smith and Vidal 1986; Stockwell *et al.* 2001; Napp *et al.* 2002). The species composition and spatial

distribution of forage fishes show dramatic differences between warm regimes and cold regimes (Bailey *et al.* 1999; Brodeur *et al.* 1999; Wyllie-Echeverria and Ohtani 1999). The water column temperatures have a great influence on the development, growth, and mortality of juvenile pollock (Napp *et al.* 2000; Blood 2002). Changes in water column temperatures also influence the growth and production of zooplankton, which in turn affect the growth and survival of larval and juvenile fishes and cause variations in the abundance of higher trophic level organisms (Coyle and Pinchuk 2002; Hunt and Stabeno 2002).

1.3.4. Nutrient cycles

The seasonal nutrient cycle was well studied during the PROBES project during the late 1970's and early 1980's. Maximal nutrient concentrations occurred just before the commencement of the spring phytoplankton bloom. After the spring phytoplankton bloom, nutrient concentrations were depleted in the surface euphotic layer, but high nutrient concentrations occurred below the pycnocline (Whitledge *et al.* 1986). Ammonium concentrations were low during spring, but high concentrations occurred below the pycnocline due to the remineralization of phytoplankton and benthic processes after the spring bloom (Whitledge *et al.* 1986). However, Stabeno *et al.* (2001) showed that episodic cross shelf advection also played an important role in supplying nutrients below the pycnocline over the middle shelf. During summer, wind event mixed the surface waters every 5-7 days and deepened the pycnocline, supplying nutrient rich bottom water into the nutrient depleted surface layer. This process increased new production in the middle shelf of the southeastern Bering Sea shelf by approximately

37% (Sambrotto *et al.* 1986). During fall and winter, vertical wind mixing gradually erodes the nutrient rich bottom layer and increases nutrient concentrations in the surface layer (Whitledge *et al.* 1986).

1.3.5. Production

There are two types of spring phytoplankton blooms over the southeastern Bering Sea shelf: ice-edge and open water blooms. An ice-edge phytoplankton bloom occurs along the receding sea ice edge, which provides cold and low salinity water and forms strong stratification (Alexander and Niebauer 1981; Niebauer *et al.* 1981). When there is no sea ice, the spring phytoplankton bloom occurs when solar radiation increases and wind mixing decreases (Sambrotto *et al.* 1986). The fate of spring production depends on the type of spring bloom. Ice-edge production tends to sink to the benthic food web due to uncoupling between phytoplankton and zooplankton, while open water spring production supports the pelagic ecosystem, due to a tight coupling between phytoplankton and zooplankton (Alexander and Niebauer 1981; Coyle and Cooney 1988; Niebauer *et al.* 1990). Continued growth of phytoplankton after the spring bloom over the middle shelf depends on additional nutrient supply into the surface euphotic layer by wind mixing events (Sambrotto *et al.* 1986).

The species composition of the dominant phytoplankton depends on the nutrient concentrations and interactions with the grazing populations. Over the outer shelf, *Phaeocystis pouchetii* is the dominant phytoplankton community at times, because large herbivores selectively graze down the diatoms. Over the middle shelf, however, small

herbivores (e.g., *Paeudocalanus* spp., *Oithona similes, and Acartia longiremis*) predominate, and they cannot graze large diatoms effectively. Thus, diatoms contribute most of the spring phytoplankton bloom over the middle shelf. Succession of dominant phytoplankton species occurs over the middle shelf due to the combination of changes in nutrient concentrations after the spring bloom and continued grazing pressure. The large long-chained diatoms change to medium sized and then to small diatoms as nutrient concentrations decrease after the spring bloom (Goering and Iverson 1981).

1.4. Recent conditions

The changes in climate over the southeastern Bering Sea shelf influence the availability of nutrients, the amount of primary production, and the allocation of carbon flux between pelagic and benthic communities in this region, by changing the wind field and the dynamics of sea ice (Niebauer *et al.* 1990; Coyle and Pinchuk 2002). The analysis of indices of the seasonal ice cover showed three different regimes, cold (1972-1976), warm (1977-1989), and intermediate (1990- 1998) during the period from 1972 to 1998 (Stabeno *et al.* 2001). Another study also showed similar regime shifts in climatic and biological indices (Hare and Mantua 2000). The first intensive studies of nutrient dynamics and primary production over the southeastern Bering Sea shelf were conducted during the early part of the warm period (1979 - 1981; Sambrotto *et al.* 1986; Whitledge *et al.* 1986).

Recently, the southeastern Bering Sea shelf experienced very unusual atmospheric conditions, related to variations of large-scale climate patterns such as the Pacific

Decadal Oscillation (PDO), El Nino Southern Oscillation (ENSO), and the Arctic Oscillation (AO). This was accompanied by variations in sea ice dynamics, local weather conditions, heat content of water column, and timing of the spring phytoplankton bloom. A recent study showed that the Bering Sea ecosystem quickly responds to atmospheric anomalies (Napp and Hunt 2001). The changes in climatic conditions are transferred to the Bering Sea ecosystem through variations in sea ice dynamics, such as the timing of advance and retreat and maximum sea ice extent (Niebauer 1988; Niebauer *et al.* 1999; Stabeno *et al.* 2001). The variation in sea ice dynamics changes the timing and fate of the spring phytoplankton bloom and eventually the dynamics of the food web, which may cause changes in the abundance of higher trophic levels (Alexander and Niebauer 1981; Niebauer *et al.* 1981; Hunt *et al.* 2002). Especially, the Oscillating Control Hypothesis relates variations in se ice dynamics to changes of timing of the spring phytoplankton bloom and subsequent changes of production and abundance of zooplankton, and explains fluctuations in higher trophic levels with the degree and direction of coupling between zooplankton and forage fish (Hunt *et al.* 2002).

1.5. Dissertation

This research was conducted as a part of several research programs: the Southeastern Bering Sea Carrying Capacity (SEBSCC) project funded by the Coastal Ocean Program (COP) of the National Oceanic and Atmospheric Administration (NOAA); the Inner Front (InFront) Study supported by the Arctic Natural Science section of the National Science Foundation, and the Summer Phytoplankton Processes project, funded under the North Pacific Marine Research Program. The first two studies included

for several field years, and aimed to develop a broad understanding of the variation in physical conditions in response to large-scale variations of climate conditions and changes in ecosystem dynamics at higher trophic levels. Last project focused on understanding of dynamics of summer phytoplankton over the middle shelf of the southeastern Bering Sea shelf.

Overall, this study aimed to provide the following information for the southeastern Bering Sea shelf ecosystem:

- the response of nutrients and primary production to the recent unusual physical conditions observed over the southeastern Bering Sea shelf;
- the spatial and temporal patterns of primary production;
- the dynamics of phytoplankton growth and nutrient utilization over the middle shelf and shelf break regions ;
- the interactions between ammonium and nitrate;
- the physiological response of summer phytoplankton when high concentrations of nutrients are supplied to the nutrient depleted surface layer of the middle shelf by wind mixing during summer.

Chapter 2 describes responses of physical (temperature, salinity), chemical (nutrients), and biological (characteristics of spring production) conditions in relation to the observed atmospheric variations during 1997, 1998, and 1999. Chapter 3 provides comprehensive data on the seasonal and spatial variation of primary production and processes governing this variation. Chapter 4 focuses on the dynamics of phytoplankton growth and nutrient

utilization over the shelf break region. Chapter 5 evaluates the existence of iron limitation using iron addition experiments preformed on water samples from the middle shelf and open ocean regions. Chapter 6 discusses the response of phytoplankton physiology when high concentrations of nutrient are added and examines the interaction between ammonium and nitrate. Chapter 7 summarizes major conclusions of this dissertation and provides suggestions for future study of nutrient and phytoplankton processes over the southeastern Bering Sea.

References

Alexander, V. and H. J. Niebauer (1981). Oceanography of the eastern Bering Sea ice-edge zone in spring. Limnology and Oceanography **26**: 1111-1125.

Askren, D. R. (1972). Holocene stratigraphic framework-southern Bering Sea continental shelf, University of Washington. 104 pp.

Bailey, K. M., D. M. Powers, J. M. Quattro, G. Villa, A. Nishimura, J. J. Traynor, and G. Walters (1999). Population ecology and structural dynamics of walleye pollock (*Theragra chalcogramma*). Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds), Fairbanks, University of Alaska Sea Grant: 581-614.

Blood, D. M. (2002). Low-temperature incubation of walleye pollock (*Theragra chalcogramma*) eggs from the southeastern Bering Sea shelf and Shelikof Strait, Gulf of Alaska. Deep-Sea Research II **49**: 6095-6108.

Brodeur, R. D., M. T. Wilson, G. E. Walters, and I. V. Melnikov (1999). Forage fishes in the Bering Sea: distribution, species associations, and biomass trends. Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds), Fairbanks, University of Alaska Sea Grant: 509-536.

Coachman, L. K. (1986). Circulation, water masses, and fluxes on the southeastern Bering Sea shelf. Continental Shelf Research **5**: 23-108.

Coachman, L. K. (1993). On the flow field in the Chirikov Basin. Continental Shelf Research **13**: 481-508.

Coachman, L. K., K. Aagaard, and R. B. Tripp (1975). Bering Strait: The regional physical oceanography. Seattle, Washington, University of Washington Press. 172 pp.

Coyle, K. O. and R. T. Cooney (1988). Estimating carbon flux to pelagic grazers in the ice-edge zone of the eastern Bering Sea. Marine Biology **98**: 299-306.

Coyle, K. O. and A. I. Pinchuk (2002). Climate-related differences in zooplankton density and growth on the inner shelf of the southeastern Bering Sea. Progress in Oceanography **55**: 177-194.

Fay, F. H. (1982). Ecology and biology of the Pacific walrus, *Odobenus rosmarus divergens* Illiger. Washington, D.C., U.S. Fish and Wildlife Service. 275 pp.

Frost, K. J. and L. F. Lowry (1981). Food and trophic relations of cetaceans in the Bering Sea. The eastern Bering Sea shelf: oceanography and resources. D. W. Hood and J. A. Calder (eds.), Vol.2, Seattle, University of Washington Press. 825-836.

Goering, J. J. and R. L. Iverson (1981). Phytoplankton distribution on the southeastern Bering Sea shelf. The eastern Bering Sea shelf: oceanography and resources. D. W. Hood and J. A. Calder (eds.), Vol.2, Seattle, University of Washington Press. 933-945.

Grebmeier, J. M., H. M. Feder, and C. P. McRoy (1989). Pelagic-benthic coupling on the shelf of the northern Bering and Chukchi Seas. II. Benthic community structure. Marine Ecology Progress Series **51**: 253-268.

Grebmeier, J. M., C. P. McRoy, and H. M. Feder (1988). Pelagic-benthic coupling on the shelf of the northern Bering and Chukchi Seas. I. Food supply source and benthic biomass. Marine Ecology Progress Series **48**: 57-67.

Hare, C. E. and N. J. Mantua (2000). Empirical evidence for North Pacific regime shifts in 1977 and 1989. Progress in Oceanography **47**: 103-146.

Hunt, G. L., Jr. and P. J. Stabeno (2002). Climate change and the control of energy flow in the southeastern Bering Sea. Progress in Oceanography **55**: 5-22.

Hunt, G. L., Jr., P. J. Stabeno, G. E. Walters, E. Sinclair, R. D. Brodeur, J. M. Napp, and N. A. Bond (2002). Climate change and control of the southeastern Bering Sea pelagic ecosystem. Deep-Sea Research II **49**: 5821-5854.

Kowalik, Z. (1999). Bering Sea Tides. Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds), Fairbanks, University of Alaska Sea Grant:93-127.

Macklin, S. A., G. L. Hunt, Jr., and J. E. Overland (2002). Collaborative research on the pelagic ecosystem of the southeastern Bering Sea shelf. Deep-Sea Research II **49**: 5813-5819.

McRoy, C. P., D. A. Hansell, A. M. Springer, J. J. Walsh, and T. E. Whitledge (1987). Global maximum of primary production in the north Bering Sea. EOS **68**: 17-27.

McRoy, C. P., D. W. Hood, L. K. Coachman, J. J. Walsh, and J. J. Goering (1986). Processes and resources of the Bering Sea shelf (PROBES): the development and accomplishments of the project. Continental Shelf Research **5**: 5-21.

Napp, J. M., C. T. Baier, R. D. Brodeur, K. O. Coyle, N. Shiga, and K. Mier (2002). Interannual and decadal variability in zooplankton communities of the southeast Bering Sea shelf. Deep-Sea Research II **49**: 5991-6008.

Napp, J. M. and G. L. Hunt, Jr. (2001). Anomalous conditions in the south-eastern Bering Sea 1997: linkages among climate, weather, ocean, and biology. Fisheries Oceanography **10**: 61-68.

Napp, J. M., A. W. Kendall, Jr., and J. D. Schumacher (2000). A synthesis of biological and physical processes affecting the feeding environment of laval walleye pollock (*Theragra chalcogramma*) in the eastern Bering Sea. Fisheries Oceanography **9**: 147-162.

Niebauer, H. J. (1988). Effects of El Nino-Southern Oscillation and North Pacific weather patterns on interannual variability in the subarctic Bering Sea. Journal of Geophysical Research **93**: 5051-5068.

Niebauer, H. J., V. Alexander, and R. T. Cooney (1981). Primary production at the eastern Bering Sea ice edge: The physical and biological regimes. The eastern Bering Sea Shelf: oceanography and resources. D. W. Hood and J. A. Calder (eds.), Vol.2, Seattle, University of Washington Press. 763-772.

Niebauer, H. J., V. Alexander, and S . M. Henrichs (1990). Physical and biological oceanographic interaction in the spring bloom at the Bering Sea marginal ice edge zone. Journal of Geophysical Research **95**: 22229-22241.

Niebauer, H. J., N. A. Bond, L. P. Yakunin, and V. V. Plotnikov (1999). An update on the climatology and sea ice of the Bering Sea. Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds.), Fairbanks, University of Alaska Sea Grant. 29-59.

NRC (1996). The Bering Sea Ecosystem, National Academy Press. 324 pp.

Reed, R. K. (1995). On the variable subsurface environment of fish stocks in the Bering Sea. Fisheries Oceanography **4**: 317-323.

Sambrotto, R. N., H. J. Niebauer, J. J. Goering, and R. L. Iverson (1986). Relationships among vertical mixing, nitrate uptake, and phytoplankton growth during the spring bloom in the southeast Bering Sea middle shelf. Continental Shelf Research **5**: 161-198.

Scholl, D. W., E. C. Buffington, and D. M. Hopkins (1968). Geologic history of the continental margin of North America in the Bering Sea. Marine Geology **6**: 279-330.

Schumacher, J. D. and R. K. Reed (1992). Characteristics of currents over the continental slope of the eastern Bering Sea. Journal of Geophysical Research **97**: 9423-9433

Schumacher, J. D. and P. J. Stabeno (1998). Continental Shelf of the Bering Sea coastal segment. The Sea. Vol. 2, A. Robinson and K. H. Brink (eds), John Wiley&Sons, Inc. : 789-821.

Smith, S. L. and J. Vidal (1986). Variations in the distribution, abundance, and development of copepods in the southeastern Bering Sea in 1980 and 1981. Continental Shelf Research **5**: 215-239.

Springer, A. M. (1998). Is it all climate change? Why marine bird and mammal populations fluctuate in the North Pacific. Biotic impacts of extratropical climate variability in the Pacific. G. Halloway, P. Muller and D. Henderson (eds), University of Hawaii: 109-119.

Springer, A. M. and C. P. McRoy (1993). The paradox of pelagic food webs in the northern Bering Sea-III. Patterns of primary production. Continental Shelf Research **13**: 575-599.

Stabeno, P. J., N. A. Bond, N. B. Kachel, S. A. Salo, and J. D. Schumacher (2001). On the temporal variability of the physical environment over the south-eastern Bering Sea. Fisheries Oceanography **10**: 81-98.

Stabeno, P. J., R. K. Reed, and J. M. Napp (2002). Transport through Unimak Pass, Alaska. Deep-Sea Research II **49**: 5919-5930.

Stockwell, D. A., T. E. Whitledge, S. I. Zeeman, K. O. Coyle, J. M. Napp, R. D. Brodeur, A. I. Pinchuk, and G. L. Hunt, Jr. (2001). Anomalous conditions in the south-eastern Bering Sea, 1997: nutrients, phytoplankton and zooplankton. Fisheries Oceanography **10**: 99-116.

Walsh, J. J. and C. P. McRoy (1986). Ecosystem analysis in the southeastern Bering Sea. Continental Shelf Research **5**: 259-288.

Walsh, J. J., C. P. McRoy, L. K. Coachman, J. J. Goering, J. J. Nihoul, T. E. Whitledge, T. H. Blackburn, P. L. Parker, C. D. Wirick, P. G. Shuert, J. M. Grebmeier, A. M. Springer, R. D. Tripp, D. A. Hansell, S. Djennidi, E. Deleersnijder, K. Henriksen, B. A. Lund, P. Andersen, F. E. Muller-Karger, and K. Dean (1989). Carbon and nitrogen cycling within the Bering/Chukchi Seas: Source regions for organic matter effecting AOU demands of the Arctic Ocean. Progress in Oceanography **22**: 277-359.

Whitledge, T. E., W. S. Reeburgh, and J. J. Walsh (1986). Seasonal inorganic nitrogen distributions and dynamics in the southeastern Bering Sea. Continental Shelf Research **5**: 109-132.

Wyllie-Echeverria, T. and K. Ohtani (1999). Seasonal sea ice variability and the Bering Sea ecosystem. Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds). Fairbanks, University of Alaska Sea Grant: 435-451.

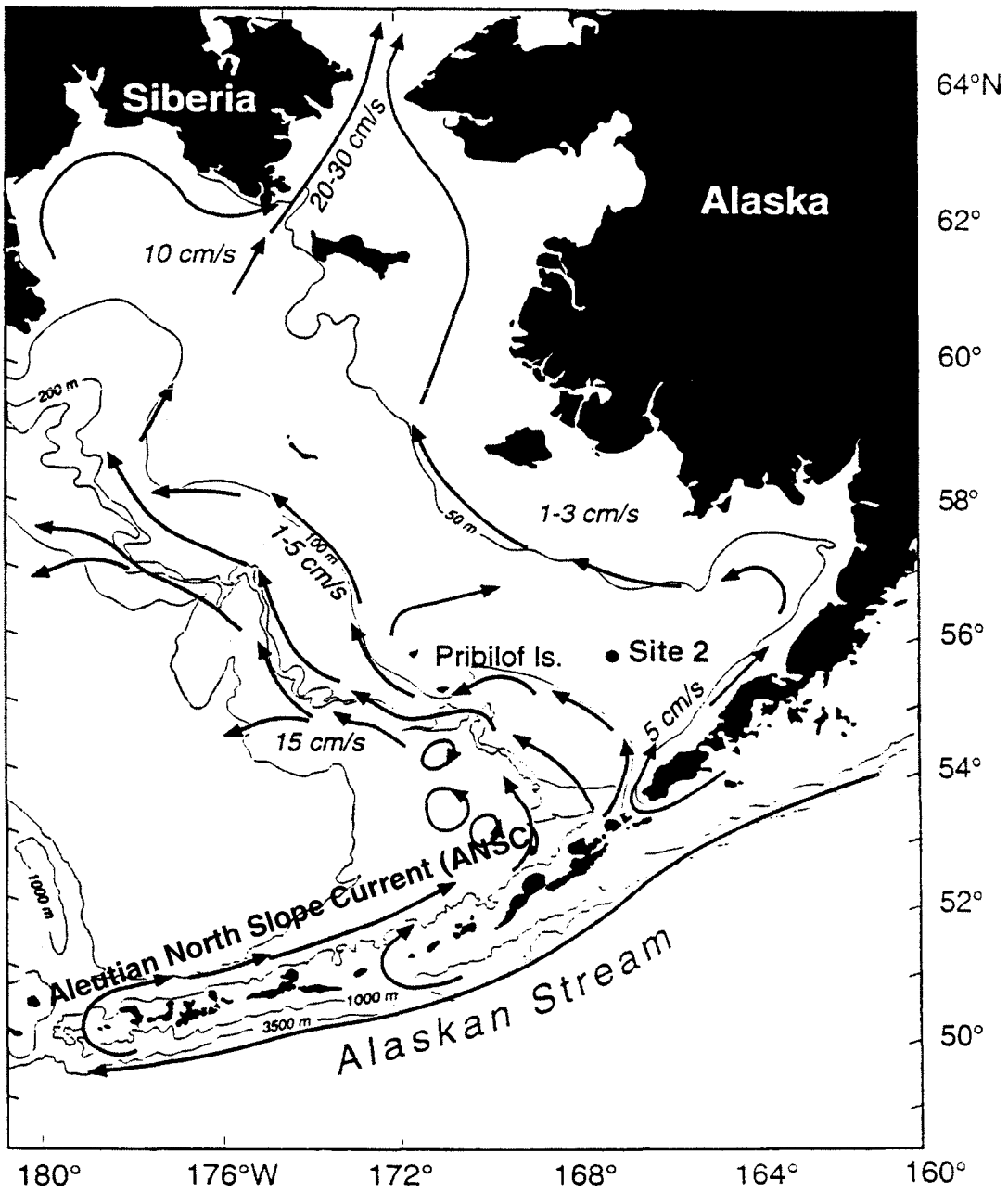

Fig.1.1. The Bering Sea and a schematic of flow on the eastern shelf in the upper 40m of the water column (After Schumacher and Stabeno 1998; Stabeno *et al.*1999).

Chapter 2. Interannual Variations of Nutrients and Primary Production Over the Southeastern Bering Sea Shelf During the Spring of 1997, 1998, and 1999

Abstract

The southeastern Bering Sea shelf experienced dramatic changes in large-scale climate conditions and local weather conditions during 1997, 1998, and 1999. We investigated the changes in nutrient distribution and primary production in response to the changing physical condition over the shelf region. Temperature and salinity profiles showed that sea ice conditions and wind-mixing events strongly influenced hydrographic conditions. Biological utilization and physical process, such as horizontal advection below the pycnocline, played an important role in the distribution and interannual variation of nutrients. The distribution of temperature and ammonium across the shelf suggested that there was offshore transport of the middle shelf water at mid-depths over the outer shelf, which may export materials from the middle shelf to the outer shelf and shelf break. The distribution of carbon and nitrogen uptake rates showed large interannual differences due to variations in the development of stratification and nutrient concentrations that resulted from variations in sea ice dynamics and wind mixing over the shelf region. The occurrence of high ammonium in early spring may affect nitrate utilization and result in an increase of total primary production.

Key words: SEBSCC, nutrients, carbon uptake rates, nitrate uptake rates, ammonium uptake rates, and southeastern Bering Sea shelf.

2.1. Introduction

The sub-arctic southeastern Bering Sea shelf is known as a very productive region for higher trophic level organisms such as crabs, fish, birds, and mammals (McRoy *et al.* 1986). During the last three decades, there have been large fluctuations in the abundance of many of these predatory marine animals. Although the causes of these fluctuations are not well understood, cumulative evidence suggests that variations in physical conditions are very important in regulating fluctuations in higher trophic level organisms by changing the dynamics of energy transfer between different trophic levels (Springer 1998).

Solar radiation, sea ice cover, and water column temperature are important controlling factors over the southeastern Bering Sea shelf. These features are closely related to the fluctuations of atmospheric conditions on various scales, from interannual to decadal and/or to longer time periods (Schumacher and Alexander 1999). The strength and position of the Aleutian Low during winter (storm tracks along the Aleutian Island chain) affect winds and surface heat flux over the southeastern Bering Sea shelf, which in turn control the extent and duration of sea ice (Niebauer *et al.* 1999; Stabeno *et al.* 2001). The variations of sea ice and wind control the development of spring blooms, with an early ice-edge bloom occurring in colder years and a later open water spring bloom in warmer years (Niebauer *et al.* 1990; Hunt and Stabeno 2002). This further affects the growth and survival of larval and juvenile fishes and recruitment of large piscivorous fish (Coyle and Pinchuk 2002; Hunt and Stabeno 2002). The location of the Aleutian Low is closely related to large-scale atmospheric variations, such as the El Nino/Southern

Oscillation (ENSO) and the Pacific Decadal Oscillation (PDO) of the North Pacific sea surface temperature (Niebauer 1988; Stabeno *et al.* 2001).

During the years of 1997, 1998, and 1999, both large-scale atmospheric conditions and local weather conditions showed a strong interannual variation over the southeastern Bering Sea shelf. In 1997, the Aleutian Low was slightly stronger than normal due to the atmospheric teleconnection of ENSO to the southeastern Bering Sea. There were strong positive solar heating anomalies from late May to mid-July and winds were generally weak, except for a severe storm in May (Overland et al. 2001; Stabeno et al. 2001). In 1998, the strength of the Aleutian Low was similar to that in 1997, but the solar heating anomalies were near zero and winds were strong into June and after mid-August (Stabeno et al. 2001). In 1999, the 1998/1999 La Niña conditions affected the North Pacific and the southeastern Bering Sea and the pattern and strength of winds were similar to those in 1998 (Freeland 2000; Stabeno 2000).

The interannual variations of physical conditions during the years of 1997, 1998, and 1999 were accompanied by unusual responses of biological and chemical conditions (Napp and Hunt 2001; Overland *et al.* 2001; Stabeno *et al.* 2001). Several anomalous conditions were observed from lower to higher trophic levels. These was a large decrease of deep nitrate concentrations during June 1997 (Stockwell *et al.* 2001), an unprecedented bloom of coccolithophores (*Emiliania huxleyi*) beginning in July 1997, and recurring in 1998 and 1999 (Hunt *et al.* 1999; Sukhanova *et al.* 1999), low returns of sockeye salmon (*Oncorhynchus nerka*) to Bristol Bay during 1997 and 1998 (Hunt *et al.*

1999), and a massive mortality of short-tailed shearwaters during 1997 (Baduini *et al.* 2001).

The purpose of this study is to describe responses of physical (temperature and salinity), chemical (nutrient), and biological (characteristics of the spring primary production) conditions to the observed atmospheric conditions during 1997, 1998, and 1999. The distribution of temperature, salinity, and nutrients were examined across the shelf and along the 70m isobath of the middle shelf of the southeastern Bering Sea. Total and new production were measured using ^{13}C and ^{15}N double labeling techniques (Slawyk *et al.*, 1977; Bury *et al.*, 1995) in order to estimate spring primary production.

2.2. Materials and Methods

Temperature and salinity data were collected over the southeastern Bering Sea shelf during early May of 1997, 1998, and 1999 (Fig. 2.1). Water samples for nutrient analyses (nitrate, silicate, phosphate, ammonium, and nitrite) were taken from Niskin bottles mounted on a CTD/rosette sampler and were analyzed on shipboard using an ALPKEM RFA model 300 automated nutrient analyzer, following Whitledge *et al.* (1981).

Water samples for productivity measurements were taken from six depths, which corresponded to the 100, 50, 30, 12, 5, and 1% penetration of the surface photosynthetically active radiation (PAR), using a CTD/rosette sampler with 5 or 10 L Niskin bottles at a morning or mid-day station. In situ light depths were determined at each productivity station using an underwater PAR sensor on the CTD frame or a secchi disk, if an underwater PAR sensor was not available. Water samples from each depth

were transferred from the Niskin bottles to a 10 L polycarbonate carboy through a 333 µm mesh net to remove large zooplankton. The water from each light depth was split into three polycarbonate incubation bottles. The incubation bottles were covered with neutral density nickel or stainless steel screens to simulate in situ light levels (i.e., 100, 50, 30, 12, 5, and 1%). Each bottle was spiked with ^{13}C ($H^{13}CO_3^-$) and ^{15}N tracers ($^{15}NO_3^-$ or $^{15}NH_4^+$) and then placed in a deck incubator cooled by running surface seawater for 4-6 hours. The addition of tracers did not exceed 10% of ambient substrate concentrations. After 4 hours, incubations were terminated by collecting particulate matter on pre-combusted GF/F glass fiber filters. The filters were kept frozen until preparation for mass spectrometric analysis. In the laboratory, the filters were acid fumed and dried for 24 hr at 60° C. Isotopic analysis for ^{13}C and ^{15}N abundance, and measurements of the quantity of particulate organic carbon (POC) and particulate organic nitrogen (PON), was performed with a CN analyzer coupled to a Europa 20-20 mass spectrometer.

^{13}C and ^{15}N uptake rates were calculated using the following equations:

Specific nitrogen uptake rates (h^{-1}) were calculated using standard JGOFS procedures (UNESCO 1994).

$$V_n = {}^{15}N_{xs} / ({}^{15}N_{enr} * t) \qquad [1]$$

Where n in V_n is the nitrogen substrate of incubation (i.e. nitrate or ammonium) and $^{15}N_{xs}$ is the excess ^{15}N [the concentration of ^{15}N (atom %) in the particulate phase after

incubation minus the natural abundance of ^{15}N (atom %) in the particulate phase (0.366%)]. t is incubation time (hrs).

$^{15}N_{enr}$ is the ^{15}N enrichment in the dissolved fraction.

$$^{15}N_{enr} = [100^* (^{15}N/ (^{15}N+^{14}N)) - ^{15}N_n] \quad [2]$$

Where ^{15}N is the concentration of labeled N, ^{14}N is the concentration of unlabelled N, and $^{15}N_n$ is the natural abundance of ^{15}N.

Absolute uptake rates (ρ, transport rates) were calculated as

$$\rho_n = PON_f * V_n \quad [3]$$

Where PON_f is the concentration of particulate organic nitrogen after incubation.

Specific carbon uptake rates (h^{-1}) were calculated using equations similar to those for nitrogen.

$$V_c = ^{13}C_{xs}/ (^{13}C_{enr} * t) \quad [4]$$

Where $^{13}C_{xs}$ is the excess ^{13}C [the concentration of ^{13}C (atom %) in the particulate phase after incubation minus the natural abundance of ^{13}C (atom %) in the particulate phase (1.108%).

$^{13}C_{enr}$ is the ^{13}C enrichment in the dissolved fraction.

$$^{13}C_{enr} = [100^* (^{13}C/ (^{13}C+^{12}C)) - ^{13}C_n] \quad [5]$$

Where ^{13}C is the concentration of labeled C, ^{12}C is the concentration of unlabelled C, and $^{13}C_n$ is the natural abundance of ^{13}C.

Absolute uptake rates (ρ, transport rates) were calculated as

$$\rho_c = POC_f * V_c \quad [6]$$

Where POC_f is the concentration of particulate organic carbon after incubation. Total CO_2 content was calculated from carbonate alkalinity that was determined from the changes of pH after addition of 25ml of 0.01N HCl into 100ml of seawater.

Daily values of productivity were estimated by multiplying hourly values by the hours of daylight (from 30 minutes after sunrise to 30 minutes before sunset). Water column uptake rates were integrated from surface to 1% light depths to obtain depth integrated areal values.

Water samples for chlorophyll were collected at each light depth and were filtered onto GF/F glass fiber filters. The filters were kept frozen and analyzed for chlorophyll-*a* by a fluorometric method following Shoaf and Lium (1976).

2.3. Results

2.3.1. Distributions of hydrographic properties

2.3.1.1. The across shelf transect

Interannual variations of spring hydrographic conditions were evident in the across-shelf temperature and salinity distributions (Fig.2.2). During early May 1997, temperature ranged from ca. –1.0 to 4° C, and salinity ranged from 31.14 to 32.76 psu. A two-layer structure over the middle shelf region was evident in the temperature profile, while a three-layer system occurred over the outer shelf region and a homogeneous water column occurred on the innermost part of the transect. The influence of ice melt water was evident by the presence of cold (-1.0 to 2° C) and relatively fresh (< 32 psu) water masses over the shelf region where the water column depth was shallower than 100m,

especially at the inner stations of the transect, around the M2 station over the middle shelf (Fig.2.2). There was a tongue-like feature of the 3° C isotherm over the outer shelf region between 30m and 80m, which may be related to the export of middle shelf water masses to the outer shelf (Fig.2.2). Warmer (> 3.5°C) and saltier (> 32.6 psu) water masses occurred in the bottom layer over the outer shelf region.

During early May 1998, the water masses over the middle and outer shelf were warmer (2°C <T< 4°C) and saltier (32 psu < S< 33 psu) than during the previous year. Over a large portion of the middle shelf area, the two-layer structure was not established. A homogeneous water mass was distributed at depths shallower than 80m over the entire shelf area. The minimum temperature over the shelf region was about 2° C, which was ca. 3°C higher than in 1997, while maximum temperatures in the bottom layer over the outer shelf were similar both years. Similar to early May 1997, warmer and saltier water masses also occurred in the bottom layer over the shelf region. However, the area that was warmer and saltier than the 4° C isotherm and the 32.7 psu isohaline was larger in 1998 than in 1997. The depth of the 33 psu isohaline was slightly shallower in 1998 than 1997. The slope of the shelf-break front was more horizontal in 1998 than in 1997, suggesting more onshore flow at the bottom layer.

During early May 1999, the ranges of temperature (-1.2°C <T<3.6°C) and salinity (31.8 psu <S<33.1 psu) were similar to those in May 1997, but the distributions were more similar to those in May 1998 (Fig.2.2). However, there was no temperature signal that would suggest the export of middle shelf water into the outer shelf. Surface temperatures over the 100m isobath showed development of stratification. Compared

with the previous two years, the distributions of temperature and salinity in the bottom layer over the shelf were slightly cooler (0.4°C) and saltier (0.2 psu) and the 33 psu isohaline occurred farther inshore over the outer shelf region in 1999. However, the slope of the shelf-break front was similar to that in 1997.

2.3.1.2. The 70m isobath transect

During early May 1997, temperature ranged from –0.9 to 1.5°C and salinity ranged from 31 to 31.6 psu (Fig. 2.3). The profiles of temperature and salinity along the 70m isobath over the middle shelf region indicated a strong influence of ice melt water, which was much more prominent in the northern part than in the southern part of the transect. There were slightly greater bottom layer temperatures and salinities, compared with the surrounding water column in the central and the southern parts of the transect. The distribution of temperature showed the development of stratification in the surface layer.

During early May 1998, temperature and salinity profiles were vertically homogeneous along the entire 70m isobath transect, and the values were greater ($0.3 < T < 2.7$°C and $31.6 < S < 32.2$ psu) than those in early May 1997. The influence of ice melt water along the 70m isobath showed a very similar pattern to that in early May 1997. During 1998, a relatively warm (> 2°C) and saline (>32 psu) water mass occurred in the water column around the 100 km region of the transect, which may be related to the intrusion of a different water mass along the 70m isobath (Fig.2.3). Along the transect, the center of intrusion of the saline water mass was displaced to the north compared with 1997, and temperature and salinity along the transect were slightly higher than in 1997.

During early May 1999, the distributions of temperature and salinity were different from the previous two years. The minimum temperature in 1999 was similar to that in 1997, but the development of stratification by surface warming was not observed. Similar to the previous two years, ice melt water occupied most of the region except for the intrusion of the warm and saline water masses in the bottom layer of the northern and southern parts of the transect. The intrusion of different water masses was slightly stronger in the north than in the south. The temperature and salinity of the invading water masses were higher and saltier in 1999 than in 1997. In 1999, temperatures were colder than in 1998, but salinities were similar to 1998.

2.3.2. Distribution of nutrients

2.3.2.1. The across shelf transect

During the spring of 1997, 1998, and 1999, the concentrations and the spatial distributions of nitrate and ammonium showed strong variations in the across shelf transects (Fig.2.4). During early May 1997, nitrate concentrations ranged from 0.5μM to 22 μM over the shelf region. Low nitrate concentrations (<1 μM) occurred in most of the surface layer (< 20m) across the shelf. However, a relatively high nitrate concentration (ca. 9 μM) occurred at the outer shelf station, where a saline water mass outcropped in the surface layer as indicated by the 32 psu isohaline. In the bottom layer of the middle shelf, nitrate concentrations were still high (> 8 μM). There were high nitrate concentrations (> 20 μM) in the bottom layer over the outer shelf. A strong gradient of nitrate concentrations, from 10 μM to 20 μM, occurred at the shelf-break front (Fig.2.4).

Ammonium concentrations ranged from 0.3 μM to 14 μM (Fig.2.4). The center of high ammonium concentrations (ca. 8-14 μM) occurred around mooring site M2, and was vertically homogeneous throughout the water column. Ammonium concentrations gradually decreased away from the M2 station and were less than 1 μM over the outer shelf region. A tongue-like structure of the 3 μM ammonium concentration occurred at about the 75m depth over the outer shelf region at the 120m isobath (Fig.2.4).

During early May 1998, nitrate concentrations were slightly higher over the entire southeastern Bering Sea shelf, compared with early May 1997, and ranged from 7 to 23 μM (Fig.2.4). Nitrate concentrations were vertically homogeneous in the upper 100m of the water column over most of the shelf region. Nitrate concentrations were low (<8 μM) in the inner end of the across shelf transect and gradually increased toward offshore stations. Nitrate concentrations were high (> 20 μM) in the bottom layer of the outer shelf.

Ammonium concentrations were greater (ca. 5- 15 μM) during early May 1998 than during early May 1997, and were vertically homogeneous. The center of high ammonium concentrations (7.5-15 μM) occurred around the 100m isobath. Ammonium concentrations gradually decreased from the center of high ammonium concentration, except that high ammonium concentrations (ca. 5-10 μM) also occurred over the shelf break region. There was also an indication of a mid-depth export of high ammonium to the outer shelf over 100m isobath (Fig.2.4).

During early May 1999, nitrate concentrations were higher (ca. 9-30 μM), but ammonium concentrations were lower (ca. 2-6 μM) over the shelf region compared with the previous two years (Fig.2. 4). Nitrate concentrations rapidly increased from 10 μM to 16 μM around the M2 station. A water mass containing high nitrate (16-20 μM) occupied most of the shelf region. There was a slight decrease of nitrate concentration in the surface layer over the outer shelf, where the water column was still well mixed to 70m. The nitrate concentration in the bottom layer over the outer shelf was higher (≥8 μM) than during the previous two years and the area with > 20 μM nitrate was greater. Ammonium concentrations over most of the shelf region were low (< 2 μM) compared to the previous two years. In the surface layer over the outer shelf, ammonium concentrations were high (ca. 6 μM), and decreased gradually away from that region (Fig.2.4).

2.3.2.2. The 70m isobath transect

During early May 1997, nitrate concentrations ranged from 0.03 to 11 μM and were depleted (< 1 μM) at most of stations along the 70m isobath over the middle shelf. The exceptions were two stations in the central part of the transect, where high nitrate concentrations occurred below 20m depth and at 40m depth near the southern end (Fig.2.5). Ammonium concentrations ranged from 0.3 to 15.4 μM along the transect. Some of the lower ammonium concentrations (< 4 μM) occurred around stations with high nitrate concentrations.

During early May 1998, nitrate concentrations ranged from ca. 8 to 15 μM and were vertically homogeneous along the 70m isobath (Fig.2.5). Along the transect, high nitrate concentrations (> 11 μM) occurred in the warmer and saltier water masses. Relatively low nitrate concentrations (< 8 μM) occurred at the southern end. Ammonium concentrations ranged from ca. 2.5 to 13.4 μM and were generally greater than 5 μM, except for a slight decrease (< 4 μM) in the bottom layer of the central part of the transect. Ammonium concentrations were higher in the south than in the north (Fig.2.5).

During early May 1999, nitrate concentrations ranged from 0.2 to 21 μM. At the northern end of the transect, depletion of nitrate (< 1 μM) occurred in the surface layer while high concentrations (> 15 μM) were found in the relatively high salinity bottom layer. Nitrate concentrations in the bottom layer were generally high in the north and decreased progressively toward the south. At the southern end, nitrate concentrations were slightly lower in the surface layer than in the bottom layer. Ammonium concentrations were generally lower (0.3-10.4 μM) than during the previous two years. High ammonium concentrations occurred in the water column between 200 km and 300 km from the southern end of the transect, coincident with the center of a cold (< -0.5° C) and less saline (< 32 psu) water mass.

2.3.3. Carbon and nitrogen uptake rates

2.3.3.1. The across shelf transect

Spring carbon uptake rates across the shelf showed interannual variations between 1997, 1998, and 1999 (Fig.2.6). During early May 1997, carbon uptake rates ranged

from 0.1 to 42.4 μg C l^{-1} h^{-1} along the across shelf transect. In the middle shelf region, two extreme carbon uptake values were observed. The lowest carbon uptake rates (< 0.2 μg C l^{-1} h^{-1}) occurred at M2 while the highest uptake rate (42.4 μg C l^{-1} h^{-1}) was observed at stations between M3 and M2, where high nutrient water outcropped in the surface layer. At the shelf break and the outer shelf regions, moderate carbon uptake rates (0.2-6.0 μg C l^{-1} h^{-1}) were observed. During early May 1998, carbon uptake rates ranged from 0.1 to 8.9 μg C l^{-1} h^{-1} across the shelf. Most of the carbon uptake rates were less than 2.5 μg C l^{-1} h^{-1}, except for the high carbon uptake rate (ca. 8.9 μg C l^{-1} h^{-1}) at the innermost station (St. 33) of the transect. The maximum carbon uptake rates in the spring of 1998 were much lower than in 1997. During early May 1999, carbon uptake rates ranged from 0.1 to 13.5 μg C l^{-1} h^{-1} along the across shelf transect. Carbon uptake rates were generally less than 5.4 μg C l^{-1} h^{-1}, but were elevated (up to 13.5 μg C l^{-1} h^{-1}) at the shelf break station. Carbon uptake rates were lower in 1999 than in 1997, but were slightly higher than in 1998.

Nitrate uptake rates in the across shelf regions also showed interannual variations during the spring of 1997, 1998, and 1999 (Fig.2.6). During early May 1997, nitrate uptake rates ranged from 0.01 to 3.8 μg N l^{-1} h^{-1} in the middle shelf region, and ranged from 0.1 to 1.4 μg N l^{-1} h^{-1} in the outer shelf and the shelf break regions. Nitrate uptake rates showed two extreme values in the middle shelf area. The minimum value occurred around station M2 and the maximum value occurred at stations between M3 and M2, where high nutrient water reached the surface. During early May 1998, nitrate uptake

rates were generally less than 0.1 μg N l^{-1} h^{-1} across the shelf, except for the innermost station (0.02-0.46 μg N l^{-1} h^{-1}) of the transect. Nitrate uptake rates were generally lower in 1998 than in 1997, in spite of higher nitrate concentrations in 1998 compared with 1997. During early May 1999, nitrate uptake rates were lower in the middle shelf region (0.02-0.25 μg N l^{-1} h^{-1}) than in the outer shelf and the shelf break regions (0.02-9.0 μg N l^{-1} h^{-1}). In general, nitrate uptake rates were higher in the across shelf transect in 1999 than during the previous two years.

Similar to nitrate uptake rates, ammonium uptake rates also varied among years. During early May 1997, ammonium uptake rates were generally less than 0.2 μg N l^{-1} h^{-1} except at station 23 (0.06-5.54 μg N l^{-1} h^{-1}) over the middle shelf. In the outer shelf and the shelf break regions, ammonium uptake rates were 0.1-0.73 μg N l^{-1} h^{-1}. During early May 1998, ammonium uptake rates were slightly higher across the shelf than during 1997. Ammonium uptake rates over the middle shelf were similar to those over the outer shelf. Ammonium uptake rates ranged from 0.6 to 2.01 μg N l^{-1} h^{-1} along the across shelf transect. During early May 1999, ammonium uptake rates across the shelf were slightly higher than during 1997, but were lower than those for 1998 (Fig.2.6).

2.3.3.2. The 70m isobath transect

The spring 1997, 1998, and 1999 carbon uptake rates varied interannually along the 70m isobath transect of the middle shelf (Fig.2.7). During early May 1997, carbon uptake rates were generally low over the middle shelf and were similar in both the southern and northern areas. During early May 1998, carbon uptake rates were slightly greater than during 1997. Carbon uptake was high in the surface layer and decreased

with depth. Carbon uptake rates in the surface layer ranged from 0.58 to 8.8 μg C $l^{-1}h^{-1}$. Carbon uptake rates in 1998 were slightly greater in the south than in the north. The highest uptake rate in 1998 occurred at station 32, located at the inner end of the transect in the southern part of the middle shelf. During early May 1999, carbon uptake rates were high in the surface layer and decreased with depth in the southern part of the transect, while carbon uptake rates showed a subsurface maximum in the northern part. Carbon uptake rates in 1999 were slightly greater than those of the previous two years. The uptake rates were higher in the north than in the south, in contrast to 1998.

Nitrate uptake rates were generally low and showed no noticeable variations in spite of the large interannual variation of nitrate concentrations along the 70m isobath (Fig.2.5; Fig.2.7). A slight increase of nitrate uptake rate was noted in the southern part of the middle shelf during the spring of 1997. However, nitrate uptake rates were much greater in the north than the south during the spring of 1999. In all years, nitrate uptake rates were highest in the surface layer and generally decreased with depth.

There were no apparent spatial differences in ammonium uptakes between the southern and northern areas, due to similar physical conditions and ammonium concentrations during 1997 and 1999 (Fig.2.7). However, in 1998, ammonium uptake rates were slightly higher in the south than in the north. Ammonium concentrations and temperatures were greater in the southern than in the northern part of the transect (Fig.2.3; Fig.2.5).

2.4. Discussion

2.4.1. Interannual variations of atmospheric and physical conditions

In response to the interannual variations of atmospheric conditions and local weather conditions, physical conditions such as the extent and duration of sea ice coverage, sea surface temperatures (SSTs), and water column average temperatures have been shown to have pronounced interannual variations. In 1997, sea ice conditions were similar to an average of the last three decades except for the timing of maximum ice extent and retreat (Stabeno *et al.* 2001). The summer SSTs were among the warmest on record since the 1960's, due to weaker winds than normal during the spring and the summer, but depth-integrated temperatures were typical of those observed during the last decade (Stabeno *et al.* 2001; Hunt and Stabeno 2002). In 1998, ice advanced to M2 and melted in February during a period of weak winds, which prevented mixing of the fresh, cold water to the bottom. After the retreat of sea ice in late February, winds were strong enough to mix the fresh, cold surface water with the warm, saline bottom water, and this resulted in the warmest depth-averaged temperatures observed in the 1990s (Stabeno *et al.* 2001). In 1999 the extent of sea ice was not different from that in 1997, but the arrival of sea ice at M2 was earlier than in 1997 and the retreat of sea ice was slow compared to the average rates of the last two decades (Stabeno 2000). The sea surface temperature and depth-averaged temperatures were also colder than those of the previous two years (Stabeno 2000).

2.4.2. Interannual variations of hydrographic conditions

Salinity and temperature over the Bering Sea shelf show strong interannual variations due to the dynamics of sea ice and winds. During winter, the extent and

duration of sea ice and wind speed and direction are major factors influencing temperature and salinity of the water column at the beginning of spring (Coachman 1986). As discussed in the previous section, interannual variations of climate and local weather conditions are probably responsible for differences in the distributions of temperature and salinity across the shelf transect and along the 70m isobath transect over the middle shelf in early May of 1997, 1998, and 1999 (Fig.2.2; Fig.2.3). Recently, data from the mooring over the middle domain in the southeastern Bering Sea shelf (M2) also confirm the important role of the timing of the advance and retreat of sea ice and the strength of winds when sea ice is advancing and retreating in regulating temperature and salinity (Stabeno *et al.* 2001). The development of stratification was greatly different among years because of the differing wind mixing in early spring. When wind mixing was weak in early May 1997, stratification developed due to melting sea ice and was evident in most of the shelf region. During early May of 1998 and 1999, however, vertically mixed waters occurred to depths of 100m (Fig.2.2; Fig.2.3).

The interannual variations of onshore fluxes play a very important role in the hydrographic characteristics over the middle shelf. The balance between the input of freshwater from melting sea ice and the input of saline water from the basin largely controls the distribution of salinity over the middle shelf (Stabeno *et al.* 2001). Salinity was similar in 1998 and 1999 but lower in 1997 (Fig.2.2; Fig.2.3). The maximum ice coverage was similar in 1997 and 1999, but salinity was higher in 1999 than in 1997. Thus, the fresh water input alone cannot explain the interannual variations of salinity. Stabeno *et al.* (2001) observed that the cross shelf transport was reduced in 1997 but

enhanced in 1998. The maximum ice coverage was slightly lower in 1998 than in 1999, but salinity was similar in both years, which may have resulted from the increased onshore transport of slope water in 1999 compared to 1998. The location of the 33m isohaline gradually moved onto the shelf from 1997 to 1998 and 1999 (Fig.2.2). As discussed later, the location of the 16 μM isopleth over the shelf also indicates an increase in onshore transport of high nitrate slope water in the shelf region (Fig.2.4).

2.4.3. Interannual variations of nitrate concentration and distribution

The spring concentrations and distributions of nitrate varied between 1997, 1998, and 1999 (Fig.2.4; Fig.2.5) in response to variations in sea ice and winds that changed nutrient utilization. Fluorescence data from the mooring indicated the occurrence of an ice related bloom in late April at the M2 site over the middle shelf (Stabeno *et al.* 2001), which presumably resulted in an extensive utilization of nutrients in the surface layer during early May 1997. However, there was no apparent increase of fluorescence in the spring of 1998 and 1999, except for an increase in early March 1999. Unfavorable physical conditions were responsible for the lack of an obvious spring bloom. There was an early retreat of sea ice (February) and strong wind mixing in early spring during 1998 and 1999 that prevented the development of density driven stratification (Stabeno *et al.* 2001).

The distributions of nitrate across the shelf were similar both in 1998 and 1999, due to strong wind-mixing events in early spring, but the concentrations of nitrate were slightly higher in 1999 than in 1998. These differences may have resulted from either a biological factor, such as phytoplankton utilization, or a physical factor, such as

interannual variations in the onshore flux of nutrient-rich slope water. Winds were strong in both 1998 and 1999, which suppressed the utilization of nitrate in both years (Fig.2.6). In spite of high nitrate concentrations within the water column, nitrate uptake rates were lower both in 1998 and 1999 than in 1997, when nitrate was depleted (Fig.2.6). High ammonium concentrations in 1998 may have reduced nitrate uptake due to ammonium inhibition, as discussed later. Therefore, we cannot explain the higher nitrate concentration in 1999 compared with 1998 based on biological consumption alone.

There may be other factors important in regulating nitrate concentrations. Another plausible mechanism for the interannual variation of nitrate concentration is a change in onshore fluxes of slope waters in the bottom layer. Stabeno and Van Meurs (1999) observed that an episodic event of onshore flow was related to an anticyclonic eddy in the southeastern Bering Sea. Recently, variations in the onshore flux of slope waters, having high nutrient concentrations and salinity, have been related to the location of eddies in the shelf regions of the Gulf of Alaska (Okkonen *et al.* 2003). As discussed earlier, the distribution of salinity suggested strong interannual variations of onshore flux during 1997, 1998, and 1999. In the across shelf transect, salinity in the bottom layer of the shelf break was higher in 1999 than in 1998, which was deduced by the farther intrusion of the 33 psu isohaline over the shelf region in 1999 than in 1998 (Fig.2.2). Salinity profiles along the 70m isobath transect also showed more extensive intrusion of high salinity and nutrient rich waters in 1999 than in 1998 (Fig.2.3; Fig.2.5). Nitrate concentrations in the bottom layer of across the shelf and along the 70m isobath sections progressively increased from 1997 to 1999.

2.4.4. Interannual variations of ammonium concentration and distribution

Whitledge *et al.* (1986) showed that ammonium concentrations were low during the initiation of the spring bloom in April and May, and increased at the beginning of June in the bottom layer over the middle shelf as a result of remineralization of the spring phytoplankton bloom. The degradation of phytoplankton increased both phosphate and ammonium concentrations, and resulted in a strong positive relationship between ammonium and phosphate concentrations (Fig.2.8). This relationship was broken when the low ammonium and high phosphate concentrations of slope water were transported onshore in the bottom layer and mixed with the shelf water mass. However, some of the data from the center of the high ammonium concentration area in 1997-1999 did not fit with the positive relationship between ammonium and phosphate. This suggests that the high ammonium concentrations may have resulted from not only the degradation of the phytoplankton bloom, but was also derived from other sources.

For instance, the high ammonium concentrations observed in the early spring of 1997, 1998, and 1999 may be related to sea ice melt waters. Most of the high ammonium concentrations occurred in the low salinity and low temperature waters formed by the ice melt, except for a high ammonium concentration band in the across shelf section during 1999 (Fig.2.2; Fig.2.4). Ammonium concentrations were higher in the ice-covered area than in the open water and increased as an ice edge bloom progressed (Niebauer *et al.* 1981). Alexander and Chapman (1981) reported that ammonium concentrations ranged from 1.4 to 4.7 μM under the sea ice and 7-22 μM in a melted sea ice core (bulk ammonium concentration of sea ice). Muller-Karger and Alexander (1987) showed that

high ammonium concentrations (5-7 μM) occurred throughout the entire water column in a transect perpendicular to the sea ice around 57 °N 165 °W during May 1982. Mock *et al.* (1997) reported that nitrogen (nitrate+ammonium) concentrations were high in ice and under-ice water, and that ca. 20-42% of total nitrogen consisted of ammonium.

Bacteria and protozoans may contribute to the high ammonium concentration, but the source of ammonium associated with melting sea ice is not well known. Niebauer *et al.* (1981) proposed that *in situ* ammonification might be responsible for high ammonium concentrations in the ice-edge zone after the onset of stratification. Muller-Karger and Alexander (1987) showed that the bacterial and flagellate community regenerated ammonium at rates up to 200% of the daily phytoplankton requirement and consumed ammonium at rates comparable to the larger phytoplankton in the Bering Sea ice-edge bloom. Mock *et al.* (1997) reported high bacterial biomass within sea ice and the underlying water in the western Baltic Sea (Kiel Bight).

The epontic algal community showed a highly patchy distribution on the underside of an ice floe in Davis Strait pack ice (Booth 1984). Primary production within the marginal ice zone showed large spatial variations due to the varying light conditions caused by changes in cloud coverage and/or ice presence (Niebauer *et al.* 1981; Muller-Karger 1984). Organic materials produced by the epontic community and the ice-edge bloom escape *in situ* grazing and sink to the bottom (Niebauer *et al.* 1981; Coyle and Cooney 1988). Muller-Karger (1984) also proposed the possibility of ammonium input from remineralization of recently settled phytoplankton cells in or close to the sediment. Similarly, Mock *et al.* (1997) suggested that, due to a cold unstratified water column in

Kiel Bight, interactions with the underlying sediment could have caused high nutrient concentrations in the water column, with decreasing concentrations from top to bottom. Nutrient concentrations within brine, normalized to the salinity of the underlying water, showed high N: P ratios, indicating a strong phosphate deficiency in ice, brine and water (Mock *et al.* 1997). The causes of the deficiency of phosphate are uncertain. When organic materials are decomposed within the sediment, ammonium and phosphate are liberated to surrounding solution. Unlike ammonium, phosphate is strongly adsorbed on ferric oxides under oxic conditions (Berner 1980). This process may result in the deficiency of phosphate.

Increased remineralization of fecal material and/or release by zooplankton as metabolic products are another possible mechanism for the unusually high ammonium concentrations observed across the shelf and along the 70m isobath in early May 1998. The relationship between ammonium and phosphate in areas with high ammonium concentrations showed that phosphate concentrations were higher than those of 1997 at similar ammonium concentrations (Fig.2.8). Because of warm water temperatures, the growth rates of zooplankton may have increased in early spring 1998, and resulted in an increase in ammonium release from metabolic processes or fecal pellet decomposition. Coyle and Pinchuk (2002) observed that the abundance and biomass of copepods increased in 1998 due to increases in water column temperature in the inner shelf of the southeastern Bering Sea. Sediment traps deployed at M2 collected more organic material in 1998 than during the other two years and fecal material was the dominant component (Smith *et al.* 2002). However, many of high ammonium concentrations were still much

higher than those expected from the relationship between ammonium and phosphate concentrations due to the remineralization of organic matter.

The interannual variation of onshore flux may also play an important role in the distribution of ammonium over the southeastern Bering Sea shelf. In 1999, most of the high ammonium concentrations followed the expected relationship between ammonium and phosphate that result from the remineralization of phytoplankton, but a negative relationship occurred in the bottom layer (Fig.2.8). As discussed earlier, the onshore flux of slope water may have been more extensive in 1999 compared with 1997 and 1998. This larger flux may have resulted in the mixing of slope water, containing high phosphate and low ammonium, with the shelf water masses, containing high ammonium, which may have resulted in a decreased ammonium concentration due to mixing with low ammonium concentration slope water. Thus the ammonium concentration before mixing may have contained higher ammonium concentrations than expected from the relationship.

2.4.5. Offshore transport of the middle shelf water under the surface mixed layer

The offshore transport of middle shelf waters, which was evident in the temperature and/or ammonium profiles across the shelf, may be a very important process for the export of production from the middle shelf to the outer shelf and shelf break regions. During early May 1997, temperature and ammonium concentrations (3°C isotherm and 3 μM ammonium isopleth) in the across shelf transect clearly showed the export of middle shelf waters at mid-depth (50-70m) to the outer shelf (Fig.2.2; Fig.2.4). During early May 1998, the export of middle shelf water to the outer shelf was not

evident in the temperature profile, but was very obvious in the ammonium profile of the across shelf transect. Whitledge *et al.* (1986) observed a tongue-like distribution of high ammonium concentrations at mid-depth (40-60m) over the outer shelf between May and June of four successive years in the late 70's and early 80's. They suggested that the tongue-like distributions of ammonium at the mid-depths of the outer shelf are associated with processes that create fine structure in the vertical profiles. Coachman and Charnell (1979) described the detailed hydrography of the outer Bristol Bay in the southeastern Bering Sea. They reported the presence of finestructure, which had net seaward movement across the outer shelf at mid-depth, between the onshore transport in the upper (0-30m) layer and the bottom layer (below 60m). They suggested that the seaward movement of the finestructure resulted from differential offshore-directed horizontal pressure gradients, produced by a progressive increase of vertical mixing landward in the middle front. It was concluded that water mass characteristics at mid-depth over the outer shelf were determined by the relative proportions of the shelf water and the slope water (Coachman 1986). Current measurements using a vertically profiling Cyclosonde conducted during the PROBES study also showed offshore flow in the bottom of the surface mixed layer (Coachman, personal communication, 1981).

Over the middle shelf, phytoplankton sink after the spring bloom and are remineralized in the bottom layer during summer (Whitledge *et al.* 1986). The supply of regenerated materials into the surface layer is slow due to strong stratification. Thus, most of the spring phytoplankton production may remain in the bottom layer of the middle shelf unless there is favorable wind forcing for mixing of the surface layer (Walsh

and McRoy 1986). However, offshore transport at mid-depth occurred during periods of low wind forcing: June for the PROBES observations (Whitledge *et al.* 1986) and this work and early May 1997 for SEBSCC (Stabeno *et al.* 2001).

The offshore transport at mid-depth may be responsible for the seaward flux of Fe (probably regenerated Fe) into the shelf break region and beyond. During summer, freshwater from river discharge is confined to the inner shelf and is transported to the north due to the existence of a strong inner front in the southeastern Bering Sea (Coachman 1986). The aeolian flux from the surrounding land into the shelf break region may be small due to the very broad shelf (> 500km). Without additional sources of Fe, phytoplankton may experience a shortage of Fe, as noted in the California coastal upwelling region (Hutchins *et al.* 1998; Hutchins *et al.* 2002). However, recent studies suggest that the growth of phytoplankton around the shelf break of the southeastern Bering Sea is not limited by the availability of Fe, although there were indications of a slight increase of chlorophyll *a* concentration in the Fe enrichment treatment compared to the control treatment (Chapter 5).

2.4.6. Interannual variations of carbon and nitrogen uptake rates

Over the southeastern Bering Sea shelf, annual rates of primary production show large interannual variations depending on the presence or absence of ice-edge blooms and strong wind events (Sambrotto *et al.* 1986; Niebauer *et al.* 1995; Hunt and Stabeno 2002). Establishment of water column stability is very important for the development of the spring phytoplankton bloom (Sverdrup 1953). Two major processes for the development of stratification in early spring over the middle shelf of the southeastern

Bering Sea are freshwater input into the surface layer by the melting sea ice and an increase of solar radiation leading to warming of the surface layer (Niebauer *et al.* 1995). The times of arrival and retreat of sea ice have been observed to be very important in controlling the occurrence of an early ice-edge related phytoplankton bloom or subsequent open water spring bloom which in turn may have significant impacts on higher trophic levels (Niebauer *et al.* 1981; Niebauer *et al.* 1995; Hunt and Stabeno 2002). The occurrences of wind mixing events are also very important for the development of the spring phytoplankton bloom and the interannual variation of annual primary production in the southeastern Bering Sea shelf (Sambrotto *et al.* 1986).

Although the maximum extent of sea ice was similar, the timing of arrival and retreat differed during 1997, 1998, and 1999. Wind mixing events also differed. The combined effects of sea ice and wind mixing resulted in interannual variations of water column stability and nutrient distributions, which caused strong interannual and spatial variations of carbon and nitrogen uptake rates (Fig.2.6; Fig.2.7). In 1997, carbon and nitrate uptake rates were very low along the 70m isobath, where nitrate was depleted in the surface layer by the ice-edge bloom in late April (Stabeno *et al.* 2001). However, carbon and nitrate uptake rates were high where high nitrate concentrations occurred in the surface layer (Fig.2.4). In spite of high nitrate concentrations, carbon and nitrate uptake rates in 1998 and 1999 were very similar to those in 1997, when nitrate concentrations were depleted. The stratification of the water column was very weak due to strong winds in late April and early May of 1998 and 1999 (Stabeno 2000; Stabeno *et al.* 2001). Our carbon and nitrogen uptake data agreed well with previous work, which

predicted the development of phytoplankton blooms as a function of the timing of arrival and retreat of sea ice in the middle shelf of the southeastern Bering Sea shelf (Alexander and Niebauer 1981; Niebauer *et al.* 1995; Hunt and Stabeno 2002).

North-south spatial distributions of carbon and nitrogen uptake rates along the 70m isobath showed strong interannual variations, due to the dynamics of sea ice and the particular location of onshore transport in each of the years. In early May 1997, there was no difference in carbon and nitrogen uptake rates between the southern and the northern parts of the middle shelf, due to the complete depletion of nutrients by the ice-edge related bloom. In early May 1998, carbon uptake rates were slightly higher in the south compared to the north, although nitrate uptake rates were very similar between the two regions. There was no apparent difference in water column stability and nitrate concentration between the two regions (Fig.2.3; Fig.2.5). However, ammonium concentrations and water column temperatures were higher in the south than in the north. Thus, the utilization of regenerated nitrogen under slightly warmer conditions could explain the observed differences. In early May 1999, there were large differences in carbon and nitrate uptake rates between the southern and northern parts of the 70m isobath (Fig.2.7). The distributions of temperature, salinity, and nutrients suggest that the development of strong stratification, caused by ice melt waters in the surface layer and the advection of high nitrate, saline waters in the bottom layer, may have resulted in an ice related phytoplankton bloom in the northern area. No bloom occurred in the southern area due to lack of stratification (Fig.2.3).

The occurrence of high ammonium concentrations in early spring may play a very important role in the utilization of nitrate and control of total production over the southeastern Bering Sea shelf. In spite of similar nitrate concentrations and stratification in 1998 and 1999, nitrate uptake rates were slightly lower in 1998 compared to 1999. High ammonium concentrations in 1998 may have inhibited the nitrate uptake rates (Wheeler and Kokkinakis 1990). In Chapter 6, the addition of ammonium in both small and large volume experiments reduced nitrate uptake rates in samples collected over the southeastern Bering Sea shelf during 2000. However, carbon uptake rates were not directly affected by the addition of different nitrogen sources. Therefore, the presence of high ammonium concentrations in early spring provides an additional nitrogen source for primary production. Ammonium inhibits nitrate uptake without affecting carbon uptake rates. The overall effect of high ammonium concentration in early spring may have resulted in an increase of total annual primary production. In support of this idea, sediment traps deployed at the M2 site showed that larger amounts of material were collected in 1998 compared with 1999, in spite of similar wind conditions (Smith *et al.* 2002).

We were unable to achieve our primary objective of assessing regional spring primary production rates in relation to different physical conditions. Unlike the PROBES periods, the development of the spring phytoplankton bloom during the 1997-1999 period showed large interannual variations due to changing dynamics of sea ice and wind mixing events. Primary production measurements were conducted over the middle shelf after the spring phytoplankton bloom during 1997 and before the spring phytoplankton

bloom during 1998 and 1999. Thus, it is very difficult to extrapolate the observed interannual variation of carbon and nitrogen uptake rates directly into the interannual variation of spring primary production. As an alternative to the direct measurement of primary production from uptake rates, we can estimate primary production based on nitrate depletion in the surface euphotic layer, C/N ratio, and f-ratio (Whitledge *et al.* 1986; Hansell *et al.* 1993). However, the estimate of total annual primary production by nitrate utilization will be too low, because high ammonium concentrations were present in early spring. In addition, the interannual variations of the onshore flux of high nitrate slope water, as observed in 1997, 1998, and 1999, and the growth of phytoplankton under the sea ice very likely contributed significantly to the variations in annual productivity (Stabeno *et al.* 1998). Nitrate uptake below the thermocline during summer may also cause underestimation of primary production using the depletion of nitrate concentration in the surface euphotic layer (Rho 2000).

2.5. Summary

The purpose of the study was to obtain spring primary production estimates and to better understand variations of the food source for zooplankton and upper trophic levels over the southeastern Bering Sea shelf during distinctively different physical conditions. Although we were unable to estimate spring primary production due to the varying and unpredictable timing of the spring phytoplankton bloom, this study provided valuable information for understanding recent changes in the dynamics of the Bering Sea shelf ecosystem, mediated by changes in physical conditions.

The timing of arrival and retreat of sea ice and wind mixing events showed strong interannual variations, which affected physical conditions such as salinity and temperature and the development of phytoplankton blooms in early spring of each year. Nutrient concentrations in early spring also showed strong interannual variation due to the variable timing of phytoplankton blooms and the onshore transport of high nutrient slope water. High ammonium concentrations in early spring of 1997 and 1998 may be related to the increased activity of zooplankton, high bacterial remineralization of organic materials due to warm water temperatures, and direct and indirect effects of melting sea ice, such as release from melting sea ice and ammonification.

Across shelf distributions of temperatures and ammonium concentrations suggest the offshore transport of water from the middle shelf to the outer shelf below the pycnocline. This may be an important mechanism for material export (including regenerated Fe) to the outer shelf and shelf break region.

During early May 1997, carbon and nitrogen uptake rates were very low in the surface water above the 70m isobath due to nutrient depletion, but were high in the outer shelf region, where nutrient concentrations remained relatively high. During early May 1998, carbon and nitrogen uptake rates were generally low in the middle and outer shelf regions, in spite of high nutrient concentrations. However, ammonium uptake rates were greater than those during the other years, because of high ammonium concentrations and warm water. During early May 1999, carbon and nitrogen uptake rates were slightly higher than during the other two years and rates were greater in the northern part of the 70m isobath transect.

To better understand the recent changes of the ecosystem dynamics in the southeastern Bering Sea, we need more information concerning the spring and annual primary production. To achieve this goal, more frequent measurements of primary production are needed in order to capture the processes of the ice-related bloom, open water spring bloom, and late summer or fall phytoplankton bloom. In addition, the continuous measurement of nitrate concentrations, using in situ moored instruments, would allow a better understanding of nitrate fluxes and improve the calculation of nitrate consumption.

References

Alexander, V. and T. Chapman (1981). The Role of epontic algal communities in Bering sea ice. The eastern Bering Sea shelf: Oceanography and resources. Vol. 2, D. W. Hood and J. A. Calder (eds). Seattle, University of Washington Press. 773-780.

Alexander, V. and H. J. Niebauer (1981). Oceanography of the eastern Bering Sea ice-edge zone in spring. Limnology and Oceanography **26**: 1111-1125.

Baduini, C. L., K. D. Hyrenbach, K. O. Coyle, A. I. Pinchuk, V. Mendenhall, and G. L. Hunt, Jr (2001). Mass mortality of short-tailed shearwaters in the Eastern Bering Sea during summer 1997. Fisheries Oceanography **10**: 117-130.

Berner, R. A. (1980). Early Diagenesis: A theoretical approach. Princeton University Press. Princeton, N.J. 237 pp.

Coachman, L. K. (1986). Circulation, water masses, and fluxes on the southeastern Bering Sea shelf. Continental Shelf Research **5**: 23-108.

Coachman, L. K. and R. L. Charnell (1979). On lateral water mass interaction -A case study, Bristol Bay, Alaska. Journal of Physical Oceanography **9**: 278-297.

Coyle, K. O. and A. I. Pinchuk (2002). Climate-related differences in zooplankton density and growth on the inner shelf of the southeastern Bering Sea. Progress in Oceanography **55**: 177-194.

Freeland, H. (2000). The state of the eastern North Pacific since autumn 1999. PICES Press **8**: 7-8.

Hansell, D. A., T. E. Whitledge, and J. J. Goering (1993). Patterns of nitrate utilization and new production over the Bering -Chukchi shelf. Continental Shelf Research **13**: 601-627.

Hunt, G. L., Jr., C. L. Baduini, R. D. Brodeur, K. O. Coyle, N. B. Kachel, J. M. Napp, S. A. Salo, J. D. Schumacher, P. J. Stabeno, D. A. Stockwell, T. E. Whitledge, and S. I. Zeeman (1999). The Bering Sea in 1998: The second consecutive year of extreme weather-forced anomalies. Eos, Transactions, American Geophysical Union **80**: 561,565-566.

Hunt, G. L., Jr. and P. J. Stabeno (2002). Climate change and the control of energy flow in the southeastern Bering Sea. Progress in Oceanography **55**: 5-22.

Hutchins, D. A., G. R. DiTullio, Y. Zhang, and K. W. Bruland (1998). An iron limitation mosaic in the California upwelling regime. Limnology and Oceanography **43**: 1037-1054.

Hutchins, D. A., C. E. Hare, R. S. Weaver, Y. Zhang, G. F. Firme, G. R. DiTullio, M. B. Alm, B. F. Riseman, J. M. Maucher, M. E. Geesey, C. G. Trick, G. J. Smith, E. L. Rue, J. Conn, and K. W. Bruland (2002). Phytoplankton iron limitation in the Humboldt Current and Peru Upwelling. Limnology and Oceanography **47**: 997-1011.

McRoy, C. P., D. W. Hood, L. K. Coachman, J. J. Walsh, and J. J. Goering (1986). Processes and resources of the Bering Sea shelf (PROBES): the development and accomplishments of the project. Continental Shelf Research **5**: 5-21.

Muller-Karger, F. and V. Alexander (1987). Nitrogen dynamics in a marginal sea-ice zone. Continental Shelf Research **7**: 805-823.

Napp, J. M. and G. L. Hunt, Jr. (2001). Anomalous conditions in the south-eastern Bering Sea 1997: linkages among climate, weather, ocean, and Biology. Fisheries Oceanography **10**: 61-68.

Niebauer, H. J. (1988). Effects of El Nino-Southern Oscillation and North Pacific weather patterns on interannual variability in the subarctic Bering Sea. Journal of Geophysical Research **93**: 5051-5068.

Niebauer, H. J., V. Alexander, and R. T. Cooney (1981). Primary production at the eastern Bering Sea ice edge: The physical and biological regimes. The eastern Bering Sea Shelf: oceanography and resources. D. W. Hood and J. A. Calder (eds.), Vol.2, Seattle, University of Washington Press. 763-772.

Niebauer, H. J., V. Alexander, and S. M. Henrichs (1990). Physical and biological oceanographic interaction in the spring bloom at the Bering Sea marginal ice edge zone. Journal of Geophysical Research **95**: 22229-22241.

Niebauer, H. J., V. Alexander, and S. M. Henrichs (1995). A time-series study of the spring bloom at the Bering Sea ice edge I. Physical processes, chlorophyll and nutrient chemistry. Continental Shelf Research **15**: 1859-1877.

Niebauer, H. J., N. A. Bond, L. P. Yakunin, and V. V. Plotnikov (1999). An update on the climatology and sea ice of the Bering Sea. Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds.), Fairbanks, University of Alaska Sea Grant. 29-59.

Okkonen, S. R., T. J. Weingartner, S. L. Danielson, and D. L. Musgrave (2003). Satellite and hydrographic observations of eddy-induced shelf-slope exchange in the northwestern Gulf of Alaska. Journal of Geophysical Research **108**: 3033.

Overland, J. E., N. A. Bond, and J. M. Adams (2001). North Pacific Atmospheric and SST Anomalies in 1997: Links to ENSO? Fisheries Oceanography **10**: 69-80.

Rho, T. K. (2000). Carbon and nitrogen uptake dynamics during 1997 and 1998 anomalous conditions in the Bering Sea. M.S. Thesis, University of Alaska Fairbanks: 95 pp.

Sambrotto, R. N., H. J. Niebauer, J. J. Goering, and R. L. Iverson (1986). Relationships among vertical mixing, nitrate uptake, and phytoplankton growth during the spring bloom in the southeast Bering Sea middle shelf. Continental Shelf Research **5**: 161-198.

Schumacher, J. D. and V. Alexander (1999). Variability and role of the physical environment in the Bering Sea ecosystem. Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds.), Fairbanks, University of Alaska Sea Grant. 147-160.

Shoaf, W. T. and B. W. Lium (1976). Improved extraction of chlorophyll-*a* and -*b* from algae using dimethyl sulfoxide. Limnology and Oceanography **21**: 926-928.

Smith, S. L., S. M. Henrichs, and T. Rho (2002). Stable C and N isotopic composition of sinking particles and zooplankton over the southeastern Bering Sea shelf. Deep-Sea Research II **49**: 6031-6050.

Springer, A. M. (1998). Is it all climate change? Why marine bird and mammal populations fluctuate in the North Pacific. Biotic impacts of extratropical climate variability in the Pacific. G. Halloway, P. Muller and D. Henderson, University of Hawaii: 109-119.

Stabeno, P. J. (2000). The status of the Bering Sea: June-December, 1999. PICES Press **8**: 2-3.

Stabeno, P. J. (2000). The status of the Bering Sea: January-July, 1999. PICES Press **8**: 2-3.

Stabeno, P. J., N. A. Bond, N. B. Kachel, S. A. Salo, and J. D. Schumacher (2001). On the temporal variability of the physical environment over the south-eastern Bering Sea. Fisheries Oceanography **10**: 81-98.

Stabeno, P. J., J. D. Schumacher, R. F. Davis, and J. M. Napp (1998). Under-ice observations of water column temperature, salinity and spring phytoplankton dynamics: Eastern Bering Sea shelf. Journal of Marine Research **56**: 239-255.

Stabeno, P. J. and P. Van Meurs (1999). Evidence of episodic on-shelf flow in the southeastern Bering Sea. Journal of Geophysical Research **104**: 29715-29720.

Stockwell, D. A., T. E. Whitledge, S. I. Zeeman, K. O. Coyle, J. M. Napp, R. D. Brodeur, A. I. Pinchuk, and G. L. Hunt, Jr. (2001). Anomalous conditions in the south-eastern Bering Sea, 1997: nutrients, phytoplankton and zooplankton. Fisheries Oceanography **10**: 99-116.

Sukhanova, I. N., H. Semina, and M. V. Venttsel (1999). Spatial distribution and temporal variability of phytoplankton in the Bering Sea. Dynamics of the Bering Sea. T. R. Loughlin and K. Ohtani (eds.), Fairbanks, University of Alaska Fairbanks Sea Grant. 453-483.

Sverdrup, H. U. (1953). On conditions for the vernal blooming of phytoplankton. Journal du Conseil. Conseil International pour l'Exploration de la Mar **18**: 287-295.

UNESCO (1994). Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements: 170 pp.

Walsh, J. J. and C. P. McRoy (1986). Ecosystem analysis in the southeastern Bering Sea. Continental Shelf Research **5**: 259-288.

Wheeler, P. A. and S. A. Kokkinakis (1990). Ammonium recycling limits nitrate use in the oceanic subarctic Pacific. Limnology and Oceanography **35**: 1267-1278.

Whitledge, T. E., D. M. Veidt, S. C. Malloy, C. J. Patton, and C. D. Wirick (1981). Automated nutrient analyses in seawater, Brookhaven National Laboratory. 216 pp.

Whitledge, T. E., W. S. Reeburgh, and J. J. Walsh (1986). Seasonal inorganic nitrogen distributions and dynamics in the southeastern Bering Sea. Continental Shelf Research **5**: 109-132.

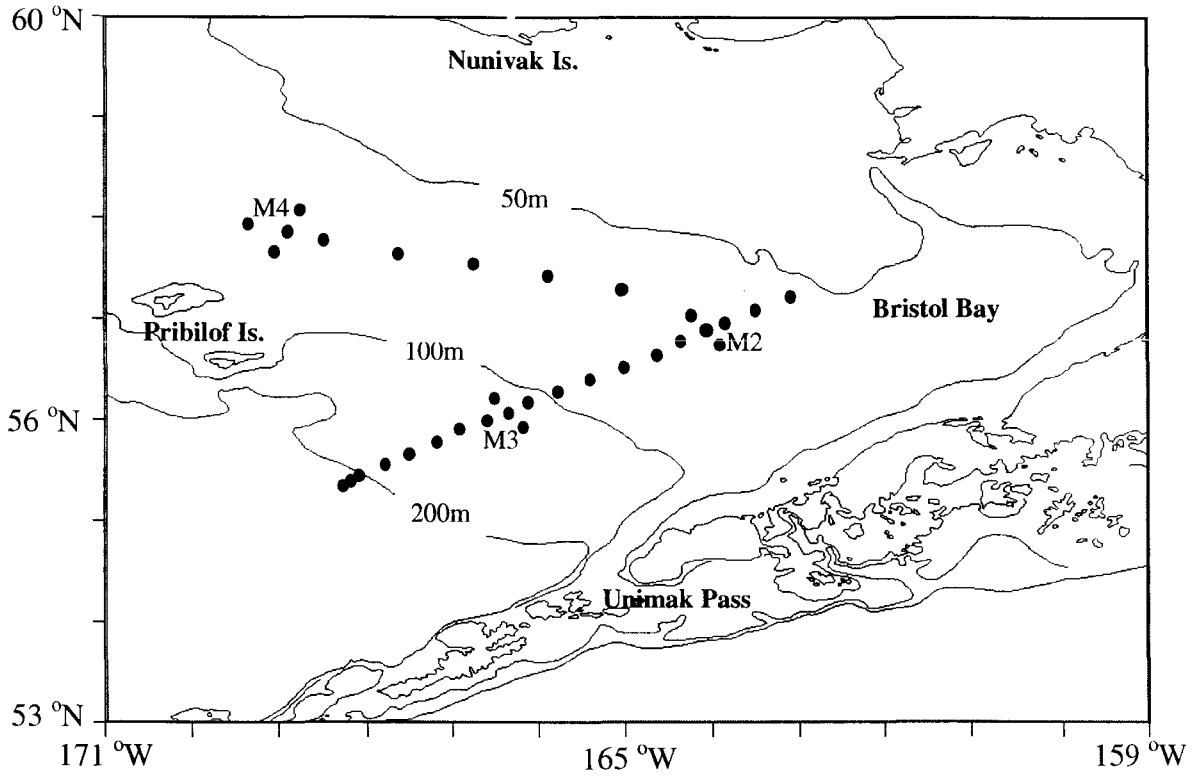

Fig.2.1. Locations of hydrographic stations across the shelf and along the 70m isobath over the southeastern Bering Sea shelf during the spring cruises of 1997, 1998, and 1999.

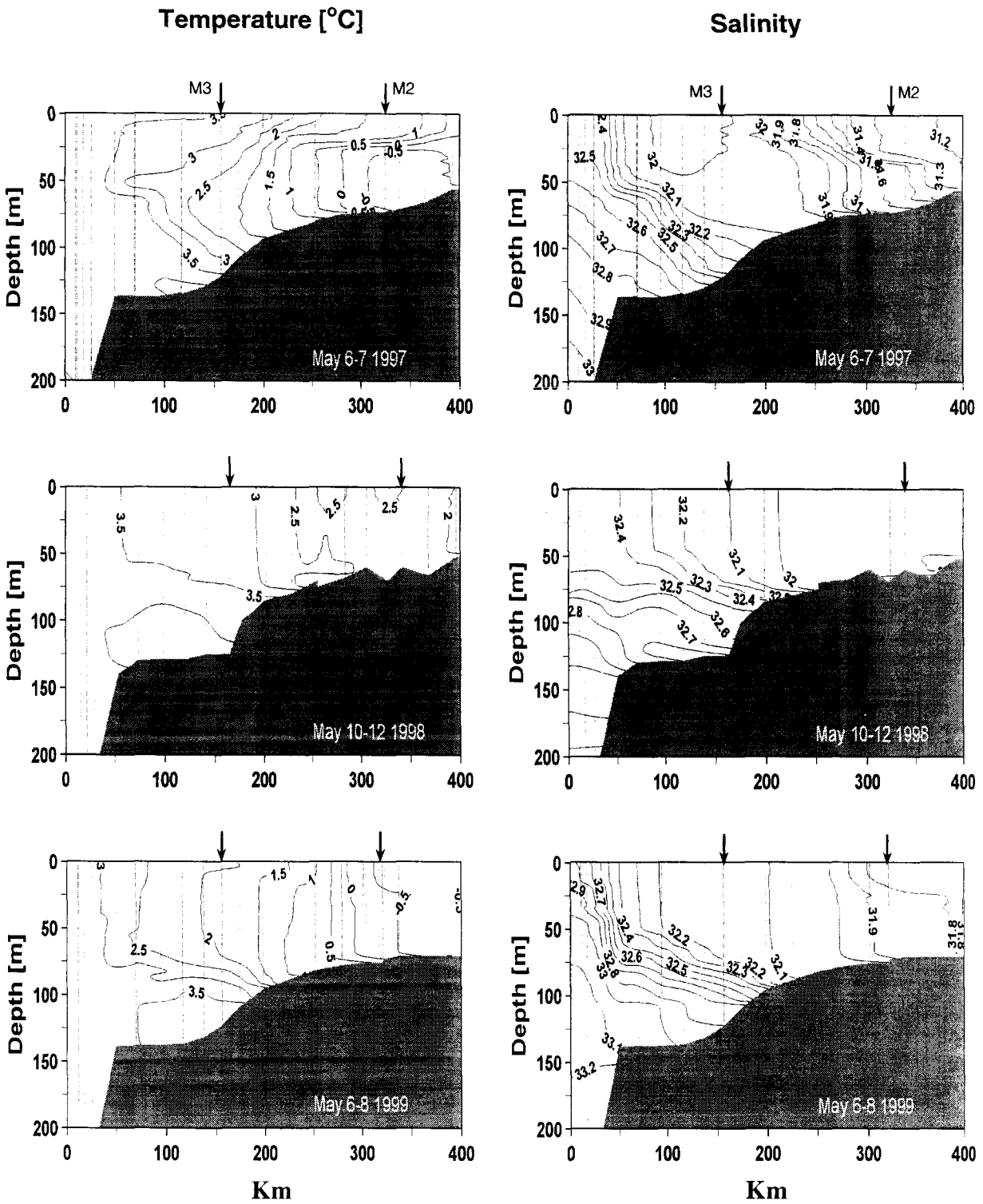

Fig.2.2. Distributions of temperature (left) and salinity (right) across the southeastern Bering Sea shelf during the spring cruises of 1997, 1998, and 1999. The locations of mooring stations are marked by arrows.

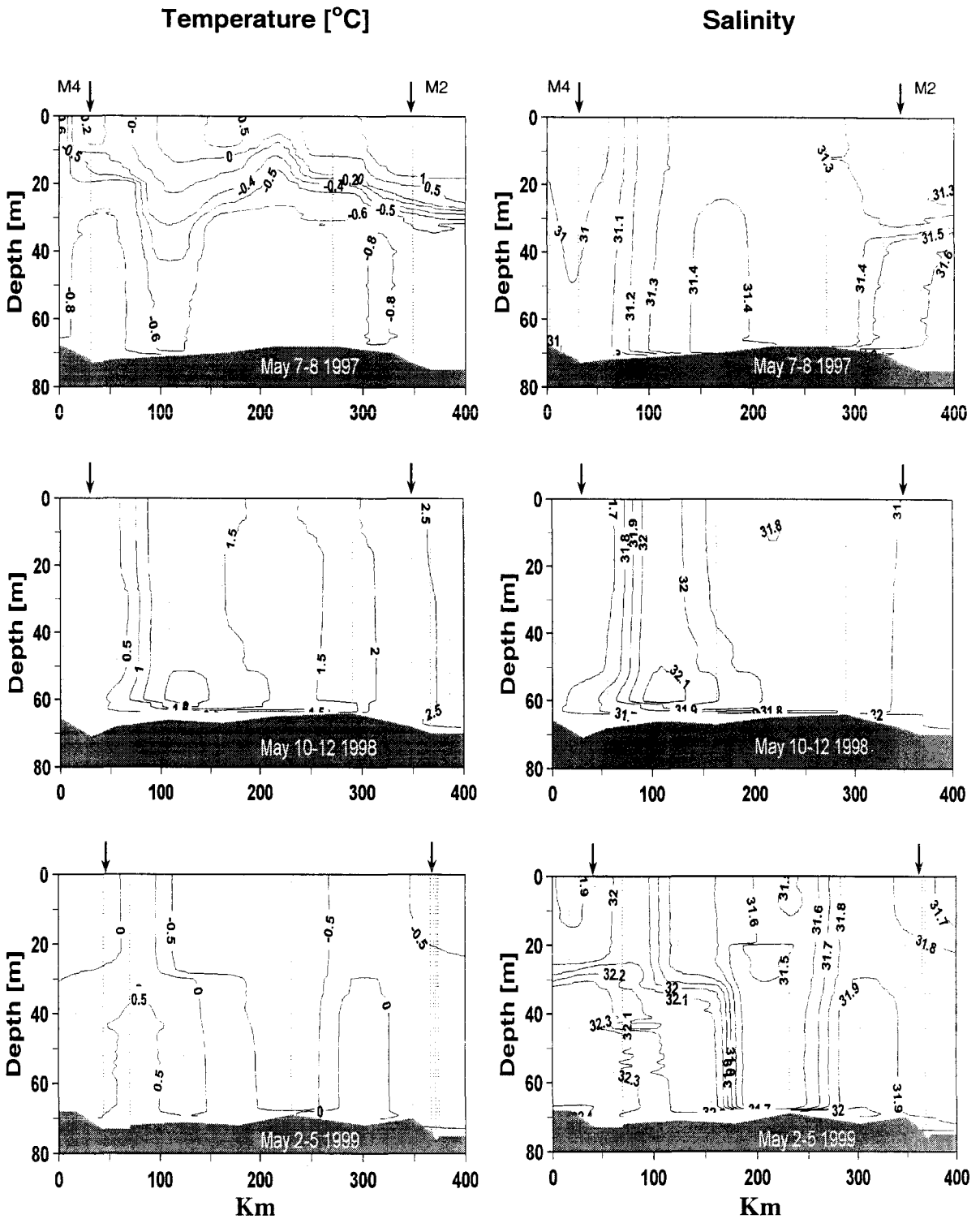

Fig.2.3. Distributions of temperature (left) and salinity (right) along the 70m isobath in the middle domain during the spring cruises of 1997, 1998, and 1999. The locations of mooring stations are marked by arrows.

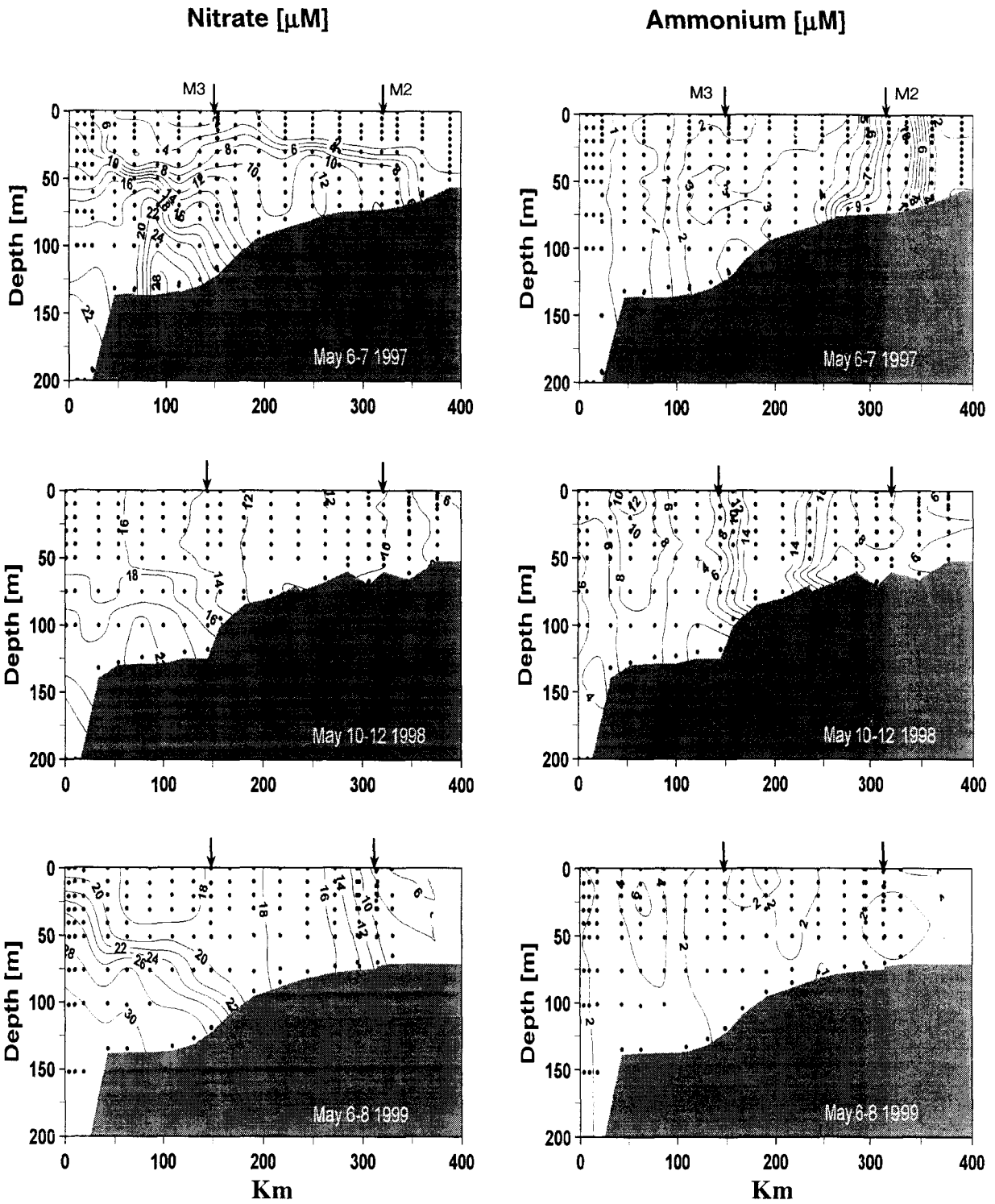

Fig.2.4. Distributions of nitrate (left) and ammonium (right) across the southeastern Bering Sea shelf during the spring cruises of 1997, 1998, and 1999. The locations of mooring stations are marked by arrows.

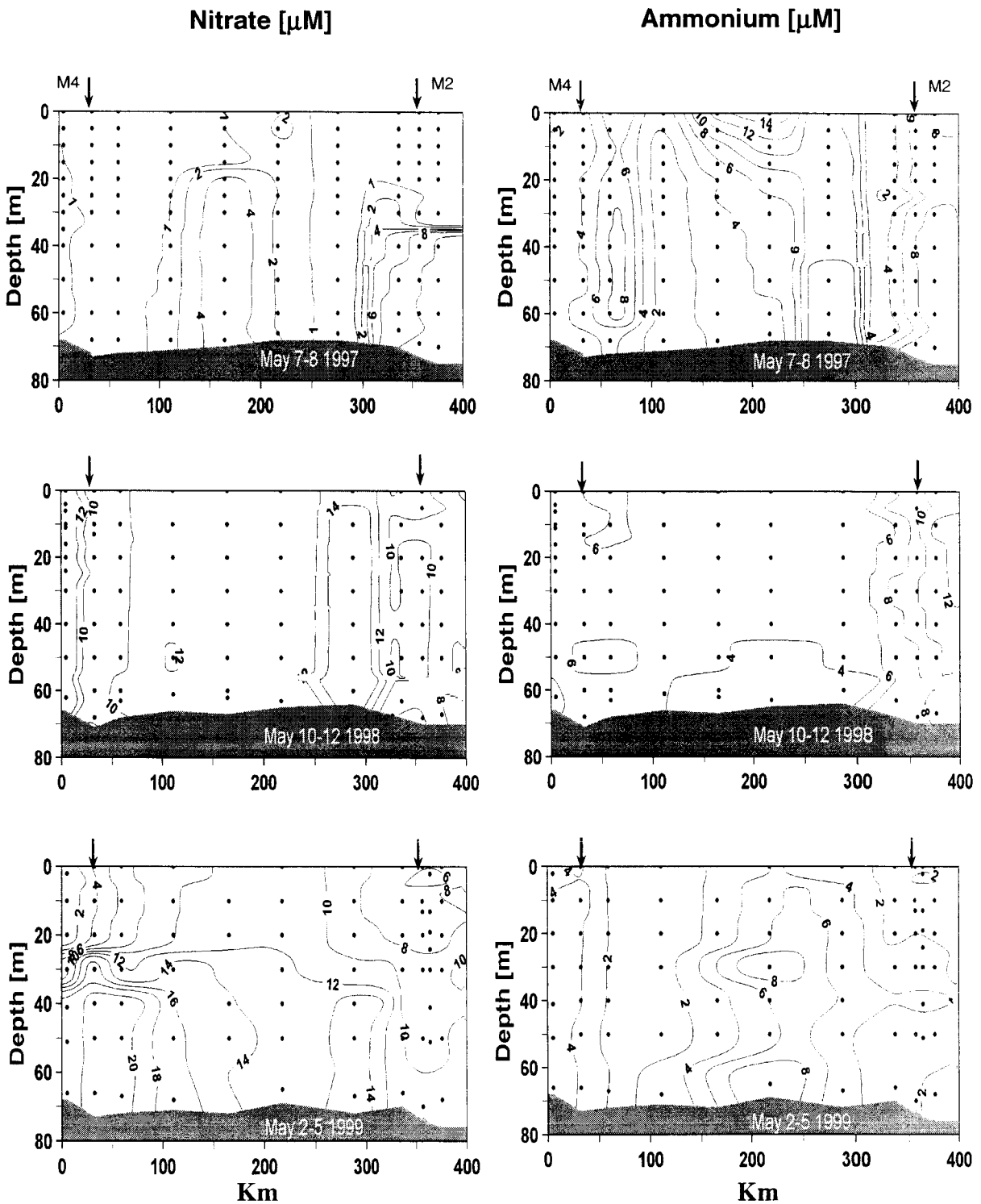

Fig.2.5. Distributions of nitrate (left) and ammonium (right) along the 70m isobath in the middle domain during the spring cruises of 1997, 1998, and 1999. The locations of mooring stations are marked by arrows.

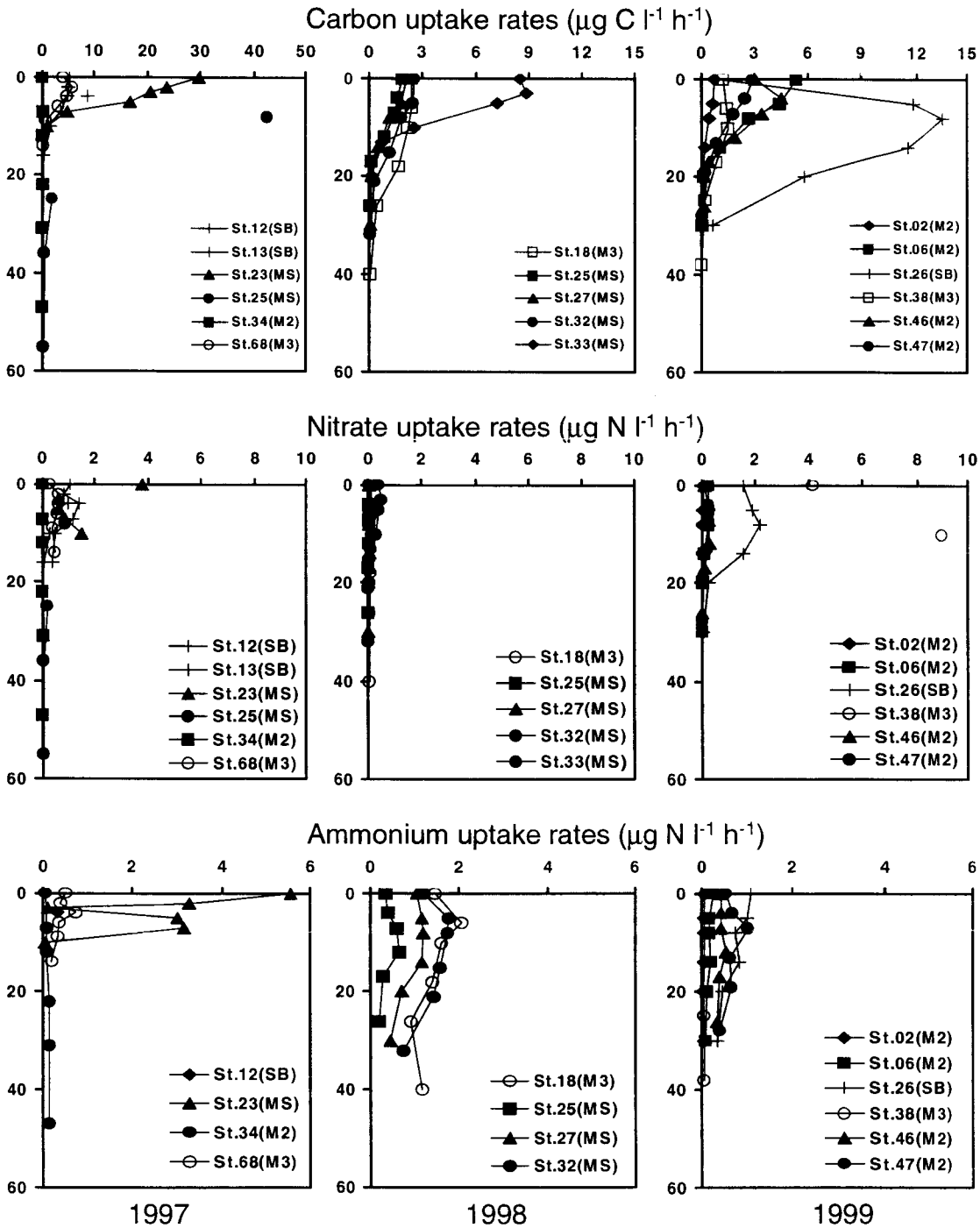

Fig.2.6. Vertical profiles of carbon, nitrate, and ammonium uptake rates from the across shelf over the southeastern Bering Sea during May of 1997, 1998, and 1999. SB indicates the shelf break region, MS stands for the middle shelf , and M2 and M3 are the locations of moorings over the shelf region.

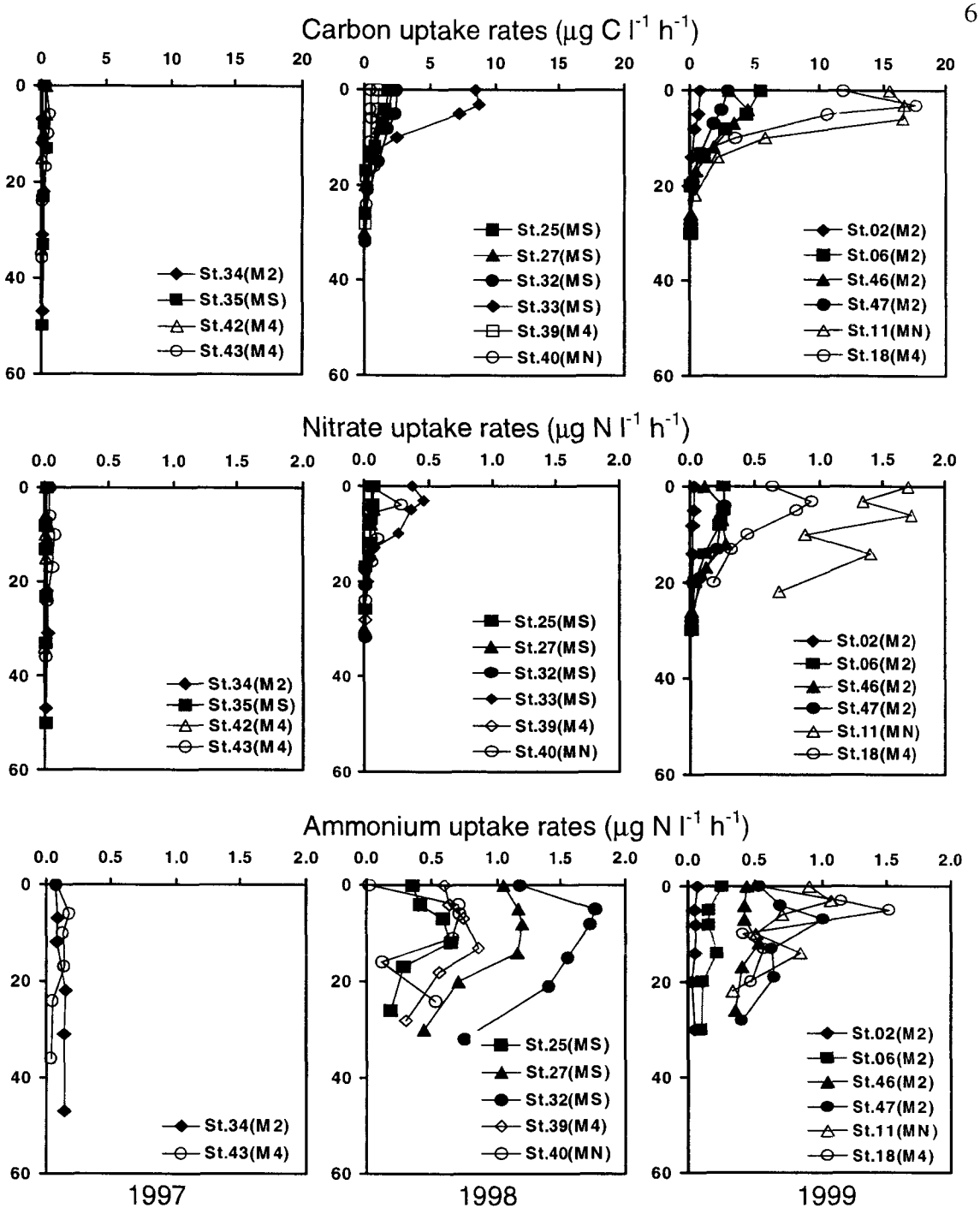

Fig.2.7. Vertical profiles of carbon, nitrate, and ammonium uptake rates along the 70m isobath over the middle shelf transect during May of 1997, 1998, and 1999. M4 and MN are located in the northern part of the middle shelf and M2 and MS are located in the southern part of the middle shelf.

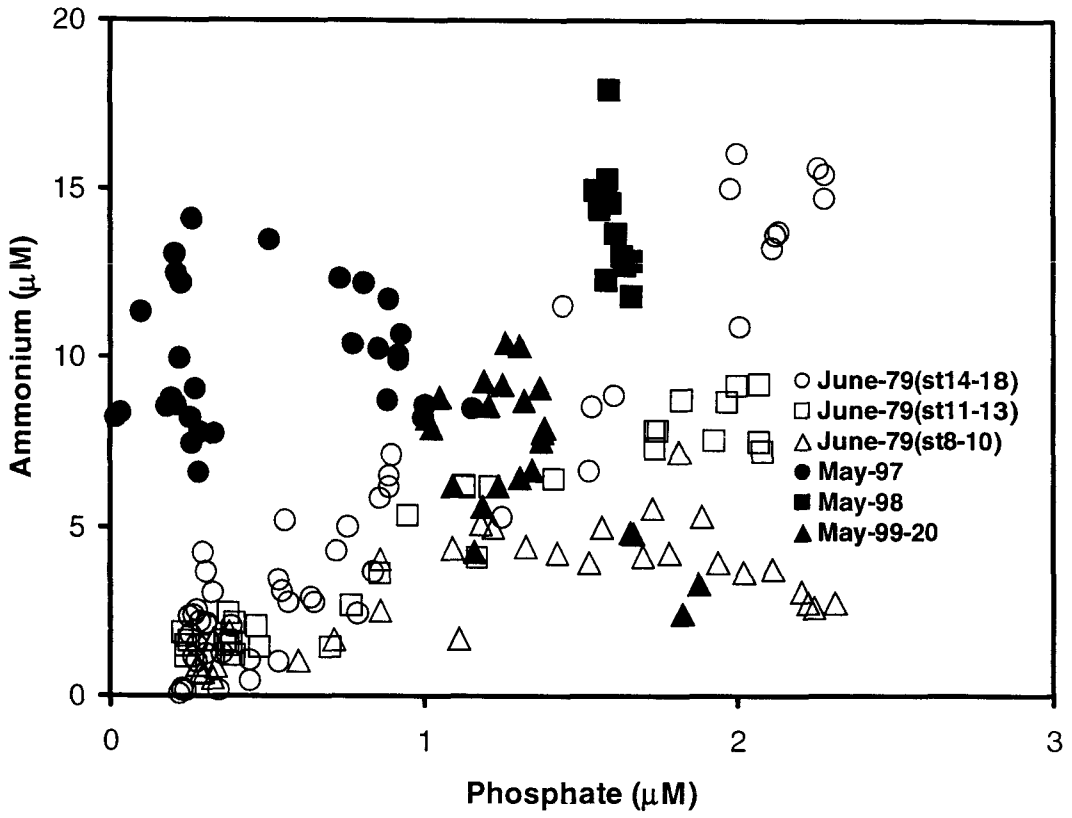

Fig.2.8. The relationship between ammonium and phosphate in the high ammonium concentration regions of the southeastern Bering Sea shelf during PROBE and this study. During PROBE, stations 14-18 were located over the middle shelf, stations 11-13 were over the middle front, and stations 8-10 were located over the outer shelf region.

Chapter 3. Seasonal and Spatial Distributions of Primary Production Over the Southeastern Bering Sea Shelf

Abstract

The Bering Sea is well known for its high productivity at upper trophic levels. Higher trophic level populations have experienced significant fluctuations in their abundance, which may be related to changes of ecosystem dynamics due to variations in physical conditions that affect primary production. Several individual studies have described the specific characteristics of the development of the spring bloom, ice edge bloom, and summer and winter blooms. However, no study has evaluated seasonal and spatial distributions of primary production, which are essential to evaluate annual rates of primary production. To better understand the seasonal and spatial distributions of primary production over the southeastern Bering Sea shelf, we analyzed ^{14}C productivity data from the Processes and Resources of the Bering Sea Shelf (PROBES) and ^{13}C productivity data from recent studies including the Southeast Bering Sea Carrying Capacity (SEBSCC) program and the Inner Front studies (IF) program. Over the entire southeastern Bering Sea shelf, primary production showed strong seasonal cycles, with a large phytoplankton bloom in spring and a small bloom in fall. Production was generally low in summer and winter due to nutrient and light limitation, respectively. Spring production contributed about 41-55% of total annual production over the shelf. The annual production in the inner shelf (133 g C m^{-2} y^{-1}) was similar to that over the middle shelf (144 g C m^{-2} y^{-1}) and the outer shelf (138 g C m^{-2} y^{-1}). This new rate for the inner shelf is higher than that previously estimated, due to the high summer and fall rates of production over the inner shelf. The maximum daily rate of productivity at the shelf

break region, ranging from 3.3 to 4.8 g C m^{-2} d^{-1}, was similar to that reported in the literature. However, the annual production (143 g C m^{-2} y^{-1}) was lower than that in the literature, due to the seasonal cycle of production. Overall, the seasonal cycle and spatial distribution of primary production showed large variations due to physical conditions such as the advance and retreat of sea ice, winds, the strength of upwelling, and the slope of the front at the shelf break that controls onshore transport of slope water in the surface and bottom layers of the outer shelf.

Keywords: primary production, southeastern Bering Sea shelf, SEBSCC, Inner Front

3.1. Introduction

The southeastern Bering Sea shelf is one of the world's most productive regions, containing abundant higher trophic level organisms including benthic and pelagic communities, sea birds, and marine mammals. Over the last few decades, the occurrence of significant fluctuations in abundance of higher trophic level organisms has been the motivation for many research activities. A change in food web dynamics, resulting from variations of climate, is one of the explanations for the fluctuations observed in this ecosystem (Springer 1998). Climate can affect both the timing and quantity of primary production. Any change in primary production will transfer through the food web, so the study of primary production is essential to understand the fluctuations in higher trophic levels.

The southeastern Bering Sea shelf is a part of the sub-arctic ecosystem that experiences strong seasonal primary production cycles, due to the dramatic change of incident radiation. This region also experiences seasonal advance and retreat of sea ice. Strong vertical stratification develops as sea ice melts, which causes an ice-edge phytoplankton bloom in early spring (Alexander and Niebauer 1981; Niebauer *et al.* 1990; Niebauer *et al.* 1995). An open water spring phytoplankton bloom occurs when sea ice is absent (Sambrotto *et al.* 1986; Whitledge *et al.* 1986). Wind mixing events are very important in maintaining production after the ice-edge or spring phytoplankton blooms (Sambrotto *et al.* 1986; Niebauer *et al.* 1995). Several primary production studies have been conducted over the southeastern Bering Sea shelf in order to understand the development of the spring bloom and the amount of primary production in the Bering

Sea. These used the ^{14}C method and indirect methods, such as assessment of nitrate depletion in the photic zone and nitrate uptake experiments (McRoy *et al.* 1972; Sambrotto *et al.* 1986; Whitledge *et al.* 1986; Hansell *et al.* 1993). However, most of the studies were focused on understanding the dynamics and the amount of production during a specific period of the year such as the ice-edge bloom (Niebauer *et al.* 1995), the spring bloom (Sambrotto *et al.* 1986; Whitledge *et al.* 1986), and the winter and summer period (McRoy *et al.* 1972). There are no year-around measurements of primary production over the complete seasonal cycle and across and along the entire shelf.

The southeastern Bering Sea shelf is very wide (> 500km width) and is divided into inner, middle, and outer shelf regions, each having unique physical, chemical, and biological conditions (Coachman 1986). There are also large spatial variations of hydrographic data (temperature, salinity, nutrient concentrations) along the 70m isobath in the middle shelf (Kachel *et al.* 2002). Primary production showed strong spatial variation across and along the shelf during the Southeast Bering Sea Carrying Capacity (SEBSCC) program and the Inner Front studies (Chapter 2). The spatial distribution of primary production over the southeastern Bering Sea shelf was not well delineated until Springer *et al.* (1996) combined most of the available primary production data from several studies. However, those measurements were collected on rather limited time and spatial scales. There were also strong interannual variations in the development of primary production, controlled by the frequency and strength of wind mixing events in early spring and the timing of sea ice retreats. Therefore, the historical primary

production measurements, with their limited temporal and spatial coverage, may have yielded an underestimate or overestimate of the actual primary productivity.

Recently, Schell (2000) suggested that there has been a decrease in the seasonal carbon fixation rate in the Bering Sea, based on a decrease of $\delta^{13}C$ in long baleen plates from bowhead whales (*Balaena mysticetus*), which feed in the northern Bering and Chukchi Sea. However, there is no apparent indication of a decrease in production over the southeastern Bering Sea shelf (Rho 2000; McRoy et al. 2001; Hunt et al. 2002). In this study, we examined the primary production data collected during the Processes and Resources of the Bering Sea Shelf (PROBES), the SEBSCC (1997-2000), and the Inner Front (1997-2000) studies to: (1) describe the seasonal cycles of primary production in the inner, the middle and the outer shelves and the shelf break regions, (2) describe the spatial variation of primary production, and (3) understand the interannual variation of primary production. This study provided a more comprehensive understanding of primary production than previous works, including greater seasonal and spatial coverage of primary production over the southeastern Bering Sea shelf.

3.2. Materials and Methods

Fig. 3.1 shows the locations of productivity measurement. Productivity was measured according to a double labeling technique using ^{15}N and ^{13}C (Slawyk *et al.* 1977) during the SEBSCC and the Inner Front studies. The procedure and calculations were described by (Rho 2000). We used the PROBES primary production data in the IMS (Institute of Marine Science) database of the University of Alaska Fairbanks, which were collected by Dr. R. Iverson using the ^{14}C method described in Goering and Iverson (1978). A comparison study showed that ^{13}C production measurements obtained by the double labeling technique are not different from ^{14}C production (Slawyk *et al.* 1977). So, we compared directly the ^{13}C measurements of this study to the ^{14}C measurements of PROBES data.

3.3. Results

3.3.1. Primary production during 1978

A seasonal cycle of primary production was evident over the southeastern Bering Sea shelf during 1978 (Fig.3.2). During 11-29 April, primary production was generally low in the outer shelf and shelf break regions and ranged from 64 to 429 mg C m^{-2} d^{-1}. However, there was high primary production at several stations located close to the Aleutian chain and ranged from 2399 to 2762 mg C m^{-2} d^{-1} with a mean of 2533 mg C m^{-2} d^{-1}. During 7- 21 May, primary production rates were low (665 mg C m^{-2} d^{-1}) until 10 May 1978 in the outer shelf regions. Primary production at stations close to the Aleutian chain was slightly less than that in April and ranged from 1329 to 2151 mg C m^{-2} d^{-1}. High primary production observed to the west of 166 °W over the southeastern Bering Sea shelf ranged from 1705 to 3203 mg C m^{-2} d^{-1}. During 27 May - 11 June, primary

production ranged from 269 to 2670 mg C m^{-2} d^{-1}. Primary production at most of the stations was lower than 600 mg C m^{-2} d^{-1}, but high primary production was observed at northern stations (2670 and 1285 mg C m^{-2} d^{-1}) and at a southern station (1581 mg C m^{-2} d^{-1}). During 20-28 June, primary production was generally low over the southeastern Bering Sea shelf and ranged from 161 to 381 mg C m^{-2} d^{-1} with a mean value of 268 mg C m^{-2} d^{-1}. Primary production was two times higher at the northernmost two stations (381 mg C m^{-2} d^{-1}) than at the southernmost two stations (190 mg C m^{-2} d^{-1}).

3.3.2. Primary production during 1979

The data Fig.3.3 show that primary production varied seasonally and spatially in 1979. During 14-25 April, primary production ranged from 405 to 1636 mg C m^{-2} d^{-1} with a mean value of 955 mg C m^{-2} d^{-1} (n=9). Primary production gradually decreased seaward and was two times higher over the middle shelf (1203 mg C m^{-2} d^{-1}, n=5) than over the outer shelf (654 mg C m^{-2} d^{-1}, n=2), in the shelf break region (684 mg C m^{-2} d^{-1}, n=1), and in the open ocean (591 mg C m^{-2} d^{-1}, n=1). During 3-20 May, primary production generally increased compared to the previous period and ranged from 743 to 4443 mg C m^{-2} d^{-1} with a mean value of 2248 mg C m^{-2} d^{-1} (n=12). Primary production was higher over the middle shelf (2858 mg C m^{-2} d^{-1}, n=6) than over the inner (1550 mg C m^{-2} d^{-1}, n=3) and outer (1727 mg C m^{-2} d^{-1}, n=3) shelves. During 25 May - 14 June, primary production ranged from 797 to 3604 mg C m^{-2} d^{-1} with a mean value of 1919 mg C m^{-2} d^{-1} (n=7). Mean primary production was lower over the middle shelf (1129 mg C m^{-2} d^{-1}, n=2) than over the outer shelf (2085 mg C m^{-2} d^{-1}, n=4) and near the shelf break (2836 mg C m^{-2} d^{-1}, n=1).

3.3.3. Primary production during 1980

The seasonal and spatial variations of primary production in 1980 are shown in Fig.3.4. During 24 March - 1 April, primary production was low across the shelf and ranged from 124 to 909 mg C m^{-2} d^{-1}, with a mean value of 350 mg C m^{-2} d^{-1}. The mean production value was three times higher over the outer shelf (593 mg C m^{-2} d^{-1}, n=3) than over the middle shelf (176 mg C m^{-2} d^{-1}, n=3) and in the shelf break region (140 mg C m^{-2} d^{-1}, n=1). During 7-23 April, primary production ranged from 196 to 1972 mg C m^{-2} d^{-1}, with a mean value of 627 mg C m^{-2} d^{-1} (n=10), which was about two times higher than that during the previous month. Production was higher over the inner shelf (772 mg C m^{-2} d^{-1}, n=1) and the middle shelf (827 mg C m^{-2} d^{-1}, n=5) than over the outer (380 mg C m^{-2} d^{-1}, n=3) and in the shelf break (221 mg C m^{-2} d^{-1}, n=1). During 28 April - 18 May, primary production was high (a mean value of 3054 mg C m^{-2} d^{-1}, n=16) and ranged from 364 to 6495 mg C m^{-2} d^{-1}. Mean primary production over the middle shelf (3722 mg C m^{-2} d^{-1}, n=8) and the outer shelf (4149 mg C m^{-2} d^{-1}, n=3) was higher than over the inner shelf (1317 mg C m^{-2} d^{-1}, n=2) and in the shelf break (1824 mg C m^{-2} d^{-1}, n=2). Primary production was lower in the northern part (364 mg C m^{-2} d^{-1}) of the middle shelf than in the southern part. During 22 May - 7 June, primary production decreased to 955 mg C m^{-2} d^{-1} (n=13), but it was greater than during 7-23 April. There was a distinctive change in primary production between late May and early June. Over the inner shelf, primary production was lower in late May (200 mg C m^{-2} d^{-1}) compared to early June (405 mg C m^{-2} d^{-1}). Over the middle and outer shelf domains, primary production was higher in late May (1413 and 1111 mg C m^{-2} d^{-1}, respectively) than in early June (679 and 431 mg C m^{-2} d^{-1} mg C m^{-2} d^{-1}). In the shelf break, primary production was higher (1968 mg C m^{-2} d^{-1}

$^{-1}$) than in other regions of the southeastern Bering Sea shelf. During 4-24 October, primary production was greater over the inner shelf (770 mg C m^{-2} d^{-1}, n=1) than the middle (215 mg C m^{-2} d^{-1}, n=1), the outer (394 mg C m^{-2} d^{-1}, n=2), and the shelf break (419 mg C m^{-2} d^{-1}, n=1) regions.

3.3.4. Primary production during 1981

The seasonal cycle in 1981 was similar to that in other years, but high production occurred in the shelf break region first (Fig.3.5). During 13-24 April, primary production was generally low and ranged from 374 to 767 mg C m^{-2} d^{-1}, with a mean value of 514 mg C m^{-2} d^{-1} (n=8). Primary production was slightly higher over the inner shelf (612 mg C m^{-2} d^{-1}, n=2) than the middle shelf (481 mg C m^{-2} d^{-1}, n=3), the outer shelf (430 mg C m^{-2} d^{-1}, n=2), and the shelf break region (582 mg C m^{-2} d^{-1}, n=1). During 30 April - 25 May, primary production ranged from 485 to 4054 mg C m^{-2} d^{-1}, with a mean value of 2037 mg C m^{-2} d^{-1} (n=16). Primary production gradually increased from the inner shelf (966 mg C m^{-2} d^{-1}, n=1) to the middle shelf (1918 mg C m^{-2} d^{-1}, n=9), the outer shelf (2138 mg C m^{-2} d^{-1}, n=3), and the shelf break (2648 mg C m^{-2} d^{-1}, n=2). During 1-20 June, primary production ranged from 207 to 1454 mg C m^{-2} d^{-1}, with a mean value of 469 mg C m^{-2} d^{-1} (n=18), which was about 23% of that the previous month. The highest primary production occurred over the inner shelf (737 mg C m^{-2} d^{-1}, n=2). Primary production decreased from the inner shelf to the shelf break (639 mg C m^{-2} d^{-1}, n=4), the outer shelf (491 mg C m^{-2} d^{-1}, n=6), and the middle shelf (298 mg C m^{-2} d^{-1}, n=6). During 27 June - 20 July, the range of primary production (from 247-1538 mg C m^{-2} d^{-1}) was similar to that in early July, but mean production was lower (456 mg C m^{-2} d^{-1}, n=19)

than that the previous month. The lowest mean primary production occurred in the inner shelf (337 mg C m^{-2} d^{-1}, n=1). Production gradually increased toward the middle shelf (346 mg C m^{-2} d^{-1}, n=8), the outer shelf (409 mg C m^{-2} d^{-1}, n=5), and the shelf break (704 mg C m^{-2} d^{-1}, n=5).

3.3.5. Primary production during 1997

During May 4-12 1997, primary production was low (204 mg C m^{-2} d^{-1}, n=6) along the 70m isobath of the middle shelf but was high (3284 mg C m^{-2} d^{-1}, n=2) between M2 and M3 (Fig.3.6). Primary production was similar in the outer shelf (601 mg C m^{-2} d^{-1}, n=1) and shelf break (579 mg C m^{-2} d^{-1}, n=6) regions (Fig.3.5). During 11-25 June 1997, low primary production extended across the entire shelf region. Primary production ranged from 28.2 to 1095 mg C m^{-2} d^{-1}, with a mean value of 201 mg C m^{-2} d^{-1} (n=23). The primary production over the inner shelf (93 mg C m^{-2} d^{-1}, n=2) and the middle shelf (105 mg C m^{-2} d^{-1}, n=8) was lower than that over the outer shelf (280 mg C m^{-2} d^{-1}, n=2) and the shelf break (328 mg C m^{-2} d^{-1}, n=9).

3.3.6. Primary production during 1998

Fig.3.6 represents the distribution of primary production during 1998. During 1-21 May 1998, primary production ranged from 205 to 1118 mg C m^{-2} d^{-1}, with a mean value of 515 mg C m^{-2} d^{-1} (n=17). Mean primary production was slightly lower over the middle shelf (467 mg C m^{-2} d^{-1}, n=8) than that over the outer shelf (608 mg C m^{-2} d^{-1}, n=4), and was similar to that at the shelf break (522 mg C m^{-2} d^{-1}, n=3) and the open ocean region (516 mg C m^{-2} d^{-1}, n=2). The highest production occurred on the inshore side of the M2 mooring site. During 20 August - 4 September 1998, most of the primary

production measurements were done over the inner shelf or the inner front region. Primary production ranged from 319 to 1219 mg C m^{-2} d^{-1}, with an mean value of 699 mg C m^{-2} d^{-1} (n=12). Primary production gradually decreased from the Slime Bank grid (994 mg C m^{-2} d^{-1}, n=3) to the Cape Newenham grid (674 mg C m^{-2} d^{-1}, n=5) and the Nunivak Island grid (509 mg C m^{-2} d^{-1}, n=4).

3.3.7. Primary production during 1999

Fig.3.7 illustrates the distribution of primary production during 1999. During 2-9 May 1999, primary production ranged from 114 to 3285 mg C m^{-2} d^{-1}, with a mean value of 1168 mg C m^{-2} d^{-1} (n=9). The highest primary production occurred over the shelf break region (3285 mg C m^{-2} d^{-1}). Mean primary production was greater over the middle shelf (973 mg C m^{-2} d^{-1}, n=7) than the outer shelf (413 mg C m^{-2} d^{-1}, n=1), due to higher production in the northern part of the middle shelf. Over the middle shelf, mean production was greater in the northern part (2082 mg C m^{-2} d^{-1}, n=2) than in the southern part (530 mg C m^{-2} d^{-1}, n=5). During 20 May - 11June 1999, most of the stations were located over the inner shelf, except for one station located over the middle shelf. Primary production ranged from 63 to 1954 mg C m^{-2} d^{-1}, with a mean value of 613 mg C m^{-2} d^{-1} (n=12). Mean production was generally lower in the Port Moller grid (108 mg C m^{-2} d^{-1}, n=2) and the Cape Newenham grid (172 mg C m^{-2} d^{-1}, n=2) than in the Nunivak grid (312 mg C m^{-2} d^{-1}, n=1) and over the middle shelf (325 mg C m^{-2} d^{-1}, n=3). The primary production in the Slime Bank grid was the highest (1378 mg C m^{-2} d^{-1}, n=4). During 23 July - 15 August 1999, primary production ranged from 148 to 1995 mg C m^{-2} d^{-1}, with a mean value of 675 mg C m^{-2} d^{-1} (n=14). Primary production was about 4-6 times greater

in the Cape Newenham grid (1064 mg C m^{-2} d^{-1}, n=2) and the Nunivak grid (1216 mg C m^{-2} d^{-1}, n=4) than in the Slime Bank grid (296 mg C m^{-2} d^{-1}, n=3) and the Port Moller grid (194 mg C m^{-2} d^{-1}, n=3). Primary production was slightly greater over the middle shelf (493 mg C m^{-2} d^{-1}, n=2) than in the Slime Bank and the Port Moller grids.

3.3.8. Primary production during 2000

The distribution of primary production during 2000 is shown at Fig.3.7. During 30 June - 17 July 2000, primary production ranged from 190 to 2710 mg C m^{-2} d^{-1}, with a mean of 1013 mg C m^{-2} d^{-1} (n=12). Production was lower over the inner shelf (190 mg C m^{-2} d^{-1}, n=1) than the middle shelf (1087 mg C m^{-2} d^{-1}, n=11). Over the middle shelf, primary production was two times higher in the northern part (1515 mg C m^{-2} d^{-1}, n=5) than the southern part (731 mg C m^{-2} d^{-1}, n=6). During 31 August -8 September 2000, primary production ranged from 57 to 1004 mg C m^{-2} d^{-1}, with a mean value of 580 mg C m^{-2} d^{-1} (n=7). Production was slightly greater over the middle shelf (751 mg C m^{-2} d^{-1}, n=2) than the outer shelf (569 mg C m^{-2} d^{-1}, n=1) and the shelf break (528 mg C m^{-2} d^{-1}, n=4).

3.3.9. Estimation of annual primary production

In this study, we estimated the annual primary production over the southeastern Bering Sea shelf by grouping all primary production data into four seasons; winter, spring, summer, and fall (Table 3. 2). Estimated annual rates of primary production were calculated to be 133 g C m^{-2} y^{-1}, 144 g C m^{-2} y^{-1}, 138 g C m^{-2} y^{-1}, 143 g C m^{-2} y^{-1}, and 31 g C m^{-2} y^{-1} for the inner shelf, the middle shelf, the outer shelf, the shelf break, and the open ocean, respectively. The fractional contributions of the spring primary production

to the annual production are 0.41, 0.55, 0.51, and 0.55 for the inner shelf, the middle shelf, the outer shelf, and the shelf break, respectively. The amount and contribution of the fall production to the total production was higher in the inner shelf than in the other regions.

3.4. Discussion

3.4.1. Seasonal cycle of primary production

Over the southeastern Bering Sea shelf, primary production shows strong seasonal cycles due to the availability of light and nutrients. During winter, in spite of high nutrient concentrations, primary production in the region is low because of the lack of light and deep mixing (McRoy *et al.* 1972). As spring approaches, insolation increases but the spring phytoplankton bloom does not develop until late April, due to a lack of stratification caused by strong wind mixing. In early May, winds decrease as the low pressure system moves away from the Bering Sea, which results in the rapid formation of surface stratification that triggers the large spring phytoplankton bloom (Sambrotto *et al.* 1986). During summer, primary production is limited by nutrient depletion, although the availability of light is favorable. The amount of summer primary production depends on the local weather conditions. Storms can disturb the surface mixed layer and bring additional nutrients into the surface layer, which may increase the amount of summer production (Sambrotto *et al.* 1986). Cloud cover also plays an important role in nutrient consumption by phytoplankton. During 1997, when vertical stratification was strong and winds were calm, a clear sky enabled deep penetration of light, which caused an increase in nitrate uptake below the pycnocline (Rho 2000). During fall, the decrease of

temperature causes weakening of stratification, which can allow the supply of nutrients to the photic zone to increase and allow the development of a second phytoplankton bloom.

Interannual variations in the seasonal advance and retreat of sea ice change the timing and fate of the phytoplankton bloom over the southeastern Bering Sea shelf. When seasonal ice advances and retreats, the input of freshwater by the melting sea ice provides buoyancy for the formation of stratification. This occurs well before the development of thermal stratification due to the increasing insolation. Stratification at the ice edge results in a phytoplankton bloom following the receding sea ice (Niebauer *et al.* 1990; Niebauer *et al.* 1995). Ice-edge production is decoupled from zooplankton grazing over the middle shelf because of the dominance of small copepods, which don't mature to feeding stages until late spring (Coyle and Cooney 1988). Thus most of ice-edge production is exported to the benthic ecosystem. When the middle shelf is ice free, the development of the spring bloom is delayed until enough buoyancy is provided by the increasing insolation. Most of the open water spring production goes to the pelagic food web, due to the tight coupling between phytoplankton and zooplankton (Coyle and Pinchuk 2002; Niebauer *et al.* 1995; Smith and Vidal 1986).

In general, our results showed a seasonal cycle of primary production similar to that observed in previous work. Primary production during the PROBES study (1978-1981), when sea ice was absent over the middle shelf, was generally low in March (176 mg C m^{-2} d^{-1}), started to increase in April (934 mg C m^{-2} d^{-1}), reached a maximum uptake rate in May (2133 mg C m^{-2} d^{-1}), and gradually decreased in June (714 mg C m^{-2} d^{-1}) and July (302 mg C m^{-2} d^{-1}). The maximum primary production usually occurred in May in

each region and gradually decreased from the middle shelf (2133 mg C m^{-2} d^{-1}) to the outer shelf (1923 mg C m^{-2} d^{-1}) and to the shelf break region (1577 mg C m^{-2} d^{-1}). This trend agreed well with temporal patterns in chlorophyll-*a*, nutrient concentrations, and nitrate uptake rates of previous studies (Sambrotto *et al.* 1986; Whitledge *et al.* 1986). During the 1997-2000 period, spring primary production (between April and May) in the middle shelf ranged from 155 to 1204 mg C m^{-2} d^{-1} with a mean value of 557 mg C m^{-2} d^{-1}, which was similar to the summer production (mean of 514 mg C m^{-2} d^{-1}) and was about 36% of the May production during the PROBES study period (Fig.3.8)

Evidence from the M2 mooring suggests that spring primary production rates were not suitably sampled during the 1997-2000 period, due to year-to-year differences in the timing of the spring phytoplankton bloom, caused by variations in advance and retreat of sea ice and wind mixing. During 1997, sea ice arrived in mid-March and retreated in mid-April at the M2 mooring site over the middle shelf and an early ice edge bloom was before our measurements. The fluorescence data collected at the M2 mooring over the middle shelf showed the occurrence of a rapid phytoplankton bloom following the receding sea ice (Stabeno *et al.* 2001). The depletion of nutrients over most of the water column also may be related to the occurrence of an ice edge bloom (chapter 2). During 1998, the advance and retreat of sea ice at the M2 mooring occurred in February, when light was insufficient for phytoplankton growth. Strong wind mixing events prevented the development of the spring phytoplankton bloom until mid May. During 1999, the advance and retreat of sea ice at the M2 site was rather sporadic. Although

there were signs of an ice edge phytoplankton bloom in late March, the spring open water phytoplankton bloom did not occur until late June (Stabeno *et al.* 2001).

3.4.2. Spatial distribution of primary production

As described in chapter 2, there are large spatial variations of hydrographic conditions, nutrient concentrations, and primary production over the southeastern Bering Sea shelf, due to the changes in the dynamics of sea ice and wind mixing. For better estimates of total annual primary production, we need good information about the seasonal cycle and the spatial distribution of primary production. The seasonal cycles of primary production over the shelf was described in the previous section. There have been several attempts to describe the spatial distribution of primary production over the Bering Sea. For instance, Springer *et al.* (1996) combined data from various sources that had differing spatial and temporal coverage. Their estimate indicates that high annual primary production occurs over the shelf break region (225 g C m^{-2} y^{-1}). The annual primary production was thought to be slightly higher over the outer shelf (143 g C m^{-2} y^{-1}) than over the middle shelf (135 g C m^{-2} y^{-1}), while low annual primary production occurred over the inner shelf (75 g C m^{-2} y^{-1}) and oceanic regions (61g C m^{-2} y^{-1}). Although there was not enough seasonal coverage to estimate annual primary production, Sorokin (1999) described the spatial distribution of primary production over the Western and central Bering Sea regions based on the ^{14}C method. The primary production of the Western Bering Sea was high in the shelf area (0.12-6.70 g C m^{-2} d^{-1}) and the Basin (0.17-4.13 g C m^{-2} d^{-1}), but low in the central Bering Sea (0.22-1.29 g C m^{-2} d^{-1}).

In this study, the spatial distribution of annual primary production in the southeastern Bering Sea shelf differed from that reported in the previous study (Springer *et al.*1996) (Table 3.2). The lowest annual primary production occurred in the open ocean beyond the shelf break (31 g C m^{-2} y^{-1}). Annual primary production was only slightly lower over the inner shelf (133 g C m^{-2} y^{-1}) than over the middle shelf (144 g C m^{-2} y^{-1}), the outer shelf (138 g C m^{-2} y^{-1}), and shelf break (143 g C m^{-2} y^{-1}). The annual primary production rates in the middle and outer shelf were very close to the estimates from other studies (Hansell *et al.* 1989; NRC 1996; Springer *et al.* 1996). However, the annual production was higher over the inner shelf and lower in the open ocean compared with that from other studies (Hansell *et al.* 1989; NRC 1996; Springer *et al.* 1996). Lowest annual primary production occurred in the open ocean, as described by earlier studies (NRC 1996; Springer *et al.* 1996), but the amount of production observed in this study was only half that of the earlier estimates. As noted in Table 3.1, production measurements in the open ocean region were collected in a very narrow time period during April and May, which may have resulted in the lower estimate of annual production in this study.

It has generally been accepted that primary production is lower over the inner shelf than the middle and outer shelves, due to the smaller nutrient reservoir (NRC 1996; Springer *et al.* 1996). However, our estimates showed that the annual production in the inner shelf was similar to that in the other regions (Table 3.2). The annual primary production for the inner shelf region was about two times higher in this study than the previous studies (NRC 1996; Springer *et al.* 1996), but there is a plausible explanation for

the high values. The previous studies did not include the contribution of summer and fall production in the estimate of the total annual production in the inner shelf region, because of the apparent complete depletion of nitrate within the water column after the spring phytoplankton bloom (Hansell *et al.* 1993). However, our uptake rates showed that production could occur utilizing regenerated nitrogen such as ammonium and urea. This was clearly shown by the high ammonium uptake rate measurements in the inner shelf regions during the summers of 1997 and 1998 (Rho 2000). As discussed earlier, the early primary production over the inner shelf may not be grazed by zooplankton, but may sink to the bottom layer and be remineralized during summer. A recent study conducted in the inner front region of the southeastern Bering Sea suggested that the inner frontal system can supply nutrients into the surface euphotic layer and can prolong primary production after the spring bloom (Kachel *et al.* 2002). Kopylov *et al.* (2002) showed that the primary production in the coastal domain around the Pribilof Islands is similar to that in the deep water area adjacent to the shelf break, due to the enhancement of nutrient supply to the surface euphotic layer by wind erosion of the thermocline.

Both the inner and middle shelf areas have not been sampled sufficiently to accurately calculate annual primary production rates, This may partly result from a slight underestimate of annual production over the middle shelf and the outer shelf due to a failure to sample the highest rates of the spring phytoplankton bloom during 1997-2000. However, the underestimate of annual production may also have happened for the inner shelf. Therefore, similar production across the shelf may not result from the

underestimate of primary production over the middle and outer shelves, but may result from the higher annual production over the inner shelf.

Springer *et al.* (1996) calculated total annual production from new production values of Hansell *et al.* (1993), ranging from 70 to 110 g C m^{-2} y^{-1}. They converted the annual new production to total annual production by multiplying f-ratio (0.4), which results in total annual production of 175 to 275 g C m^{-2} y^{-1}. The estimation of new production was calculated from estimates of nitrate consumption. Since the nitrate consumption was calculated by subtracting summer nitrate concentrations from end-of – winter nitrate concentrations (Hansell *et al.* 1993), the new production estimates may include better seasonal variations during the spring phytoplankton bloom. However, most of new production estimates of Hansell *et al.* (1993) were 70 g C m^{-2} y^{-1} with a single high value (110 g C m^{-2} y^{-1}). Springer et al. (1996) used the mid-point of the range from 175-275 g C m^{-2} y^{-1}(225 g C m^{-2} y^{-1}), which, therefore, could have resulted in overestimation of annual primary production in the shelf break region.

Although the maximum daily rate of primary production in this study (4.05 g C m^{-2} d^{-1} during 30 April 1981) was similar to that of Kopylov *et al.* (2002) in the shelf break region, a high rate of annual primary production in this region was not apparent in our data (Table 3.2). As discussed in the previous section, primary production in the shelf break region was shown to have seasonal cycles like those of the middle and outer shelves during 1980 and 1981 (Fig.3.8), and there were differences in the timing of the development of the phytoplankton bloom across the shelf. Therefore, the lack of primary production measurements covering the entire seasonal cycle of annual primary

production could have resulted in overestimation or underestimation of annual primary production in the shelf break region. However, the estimate of annual primary production in this study included the mid-summer data, which may have prevented the overestimation of annual primary production using only high daily rate of primary production values from spring and early summer.

The temporal sequence of the development of the phytoplankton bloom across the shelf showed that the phytoplankton bloom started in the inner shelf and moved to the middle shelf, the outer shelf, and the shelf break, progressively (Fig.3.3, Fig.3.4, and Fig.3.9). Over the inner shelf, the growth of phytoplankton may be less influenced by the development of stratification. Light may penetrate to a large portion of the shallow inner shelf (<50m), which may allow the growth of phytoplankton without the development of strong stratification. Recent observations over the middle shelf show that phytoplankton can grow rapidly under the sea ice (Stabeno *et al.* 1998). Therefore, low light conditions over the inner shelf may not prevent the development of phytoplankton growth in late winter or early spring. The chlorophyll-*a* data showed that high concentrations occurred over the inner shelf (2.5 to 18.9 mg Chl-*a* m^{-3}) during 11-13 April 1981, while low concentrations (0.53-0.9 mg Chl-*a* m^{-3}) occurred over the other parts of the across shelf transect. However, there were no high primary production rate data in Fig.3.9, because primary production measurements were collected too late in the season to observe the bloom.

Sambrotto *et al.* (1986) showed that the spring phytoplankton bloom occurs when solar insolation increases and wind mixing decreases over the shelf. They described the

mechanism for the initiation of spring phytoplankton blooms from time series measurements of hydrographic conditions, chlorophyll-*a* and nutrient concentrations, and nitrate uptake rates at station 12 of PROBES main sampling transect over the southeastern Bering Sea. Therefore, their work did not describe the varying times of the development of the spring phytoplankton bloom across the shelf. However, Whitledge *et al.* (1986) described the temporal sequence of the development of the spring phytoplankton bloom across the shelf, and noted that integrated amounts of chlorophyll biomass were related to increases in vertical stratification.

There were spatial differences in the timing of the spring bloom across the shelf during the PROBES study (Fig.3.9), which could be attributed to the influence of sea ice melt water (chapter 2). Over the middle shelf, when seasonal ice occurs, the input of freshwater by melting sea ice provides buoyancy for the development of stratification. An ice edge bloom occurs following the retreating sea ice, which may result in an earlier phytoplankton bloom over the middle shelf than over the outer shelf and the shelf break (Niebauer *et al.* 1995).

However, sea ice did not advance over the middle shelf during the PROBES study. Even so, less saline sea ice melt water might still have influenced the hydrographic conditions over the shelf regions. Coachman (1986) observed a salinity minimum at the offshore edge of the middle shelf and attributed it to the advection of ice melt water by the wind. Hydrographic data (temperature and salinity) collected between late March and mid April of 1980, showed that a lens of relatively fresh water (< 32.0 psu) occurred in the surface layer near the 100m isobath, which increased water column

stability (Fig.3.10). The location of high chlorophyll-*a* concentrations during 11-13 April 1980 coincided with this lens of relatively fresh water.

The progression of the spring bloom beyond the shelf break was closely related to the strength of upwelling and the slope of the front at the shelf break. The temperature and salinity distribution showed that the slope of the front at the shelf break was nearly vertical during 24-26 March 1980, and strong upwelling occurred outside of the shelf break as indicated by surfacing of the 33 isohaline. During 11-13 April 1980, the strength of upwelling decreased as indicated by deepening of the 33 isohaline. This may result in the onshore transport of warm and saline water in the surface layer as indicated by the 3° C isotherm and the 32.5 psu isohaline, as well as in the bottom layer, as indicated by the location of the 33 psu isohaline over the outer shelf (Fig.3.10). The advection of warm and saline water may be responsible for the strengthening of the stratification, which was established by the input of low salinity water in the surface layer over the shelf. Stabeno *et al.* (1998) reported that the development of stratification by the advection of saline, warm slope water in the bottom layer of the middle shelf occurred before the input of buoyancy by the melting ice.

The strength and the slope of the front at the shelf break play a very important role in the concentration and spread of phytoplankton cells in the surface layer over the shelf regions. When the slope of the front at the shelf-break relaxed, the exchange of water column properties from the outer shelf to the shelf break regions increased. The steep and strong front at the shelf break, as indicated by the 3°C isotherm and the

surfacing of the 33 psu isohaline, prevented the exchange of properties in the surface layer and confined the phytoplankton bloom to the shelf regions (Fig.3.11).

There were also latitudinal differences of phytoplankton development in the southeastern Bering Sea. During 1978, high primary production initially occurred in the southern part (Fig.3.2B), but later in the season (late May- late June), primary production was low in the southern part while high production occurred in the northern part (Fig.3.2C and D). During the spring bloom of 1980, primary production was high in the southern part, while low primary production occurred in the northern part (Fig.3.5C). During early May of 1999, primary production was higher in the northern part than in the southern part of the middle shelf (Fig.3. 7A). If sea ice advanced to the middle shelf, there might be temporal differences in the retreat of sea ice between the southern and the northern parts, which could result in the temporal variation of the development of the phytoplankton bloom following the receding sea ice.

However, this process would not explain the meridional differences in the primary production over the middle shelf during the PROBES studies, when sea ice was not present. The spatial variation of the onshore transport of nutrient rich saline slope water in the bottom layer could have caused the differences in the northern and southern areas of the middle shelf. In chapter 2, there were interannual variations in locations of saline water intrusion along the 70m isobath in the middle shelf. The intrusion of saline slope water in the bottom layer reinforces the stabilization of the water column, which has been initiated by the melting sea ice (Stabeno *et al.* 2001).

3.4.3. Interannual variations of primary production

Recently, long term monitoring of temperature and fluorescence over the middle shelf (M2) of the southeastern Bering Sea has shown that there are large interannual variations in the timing of sea ice advance and retreat (Stabeno *et al.* 2001). These produce large changes in phytoplankton bloom development that fall into two broad categories: early ice edge blooms and late open water spring blooms (Hunt and Stabeno 2002). The interannual variation of primary production could result from the changes in coupling between phytoplankton and zooplankton caused by temperature (Table 3.1). Interannual variations of primary production also occur due to wind mixing events after the ice-edge or the open ocean spring blooms. Primary production during the spring phytoplankton bloom was higher in 1979 and 1980 than in 1981 (Table 3.1). Wind mixing events were more frequent in 1979 and 1980 than in 1981, which may have supplied more nitrate to the surface euphotic layer and may have supported more production during the post bloom periods of 1979 and 1980 (Sambrotto *et al.* 1986). If wind-mixing events occurred during the peak bloom period, this could have decreased peak bloom production, although total annual primary production would have increased due to an increase in the nutrient supply. Therefore, the peak bloom production should have been similar or greater in 1981 (under calm conditions) compared with 1979 and 1980 (under stormy conditions). However, the primary production over the middle shelf during the spring bloom was lower in 1981 than in 1979 and 1980 (Table 3.1). The integrated chlorophyll-*a* concentrations showed the same trend as primary production (Sambrotto *et al.* 1986; Smith and Vidal 1986).

Several studies have shown that the growth rate of zooplankton is closely related to the temperature of the water column. Water column temperature was higher in 1981 than 1980, which resulted in a higher abundance of *Pseudocalanus spp.* and *Calanus marshallae* in 1981 than in 1980 (Smith and Vidal 1986; Coyle and Pinchuk 2002; Hunt and Stabeno 2002). Thus, the tight coupling between phytoplankton and zooplankton may be responsible for the lower rate of primary production and chlorophyll-*a* concentration in 1981 than in 1980 (Smith and Vidal 1986).

There were also interannual variations in the temporal sequence of the development of phytoplankton. The spring bloom occurred earlier over the middle shelf than over the outer shelf and the shelf break during 1978-1980, but the trend was reversed in 1981 (Fig.3.9). The initiation of the spring bloom in 1981 was very similar to that in 1980, except for the high chlorophyll-*a* concentrations on the inner side of the across shelf transect (Fig.3.12). However, the amount of onshore transport of warm and saline slope water was much smaller in 1981 than in early spring of 1980 as indicated by the location of the 33 psu isohaline at the shelf break in Fig.3.12. Increased onshore transport resulted in warmer water masses and allowed the development of stratification in the surface layer over a more extensive area, from the outer shelf to the shelf break region. Hence, temporal variations of the spring phytoplankton bloom across the shelf were apparently related to the strength and the slope of the front at the shelf break region that influenced the amount of onshore transport in the bottom layer.

3.5. Summary and conclusion

The rates of primary production in the southeastern Bering Sea shelf showed a strong seasonal cycle due to the strong seasonal variation of light and nutrients. Primary production was low in late winter, reached a maximum rate in spring, decreased gradually as summer approached, and showed a slight increase in fall. The development of the spring phytoplankton bloom depended on the stability of the water column that was established by increased insolation and fresh water input from ice melt, decreased wind mixing, and the onshore transport of warm saline water in the surface layer as well as in the bottom layer.

The spatial distribution of annual primary production showed a somewhat different pattern than that described by Springer *et al.* (1996). Our study showed that annual primary production was similar over the inner, the middle and the outer shelves and the shelf break. The lowest annual production occurred in the open ocean. Over the middle and the outer shelves, the annual production was similar to that reported in the literature (McRoy *et al.* 1986; Springer *et al.* 1996), in spite of the lack of spring bloom measurements in the recent study (1997-2000). However, there were large differences in rates for the inner shelf, the shelf break, and the open ocean, which may have resulted from insufficient seasonal and spatial measurements of primary production. The development of the phytoplankton bloom started over the inner shelf and gradually progressed to the middle shelf, the outer shelf, and the shelf break. There was also a latitudinal difference in the development of the spring phytoplankton bloom over the middle domain of the southeastern Bering Sea shelf, which could be related to temporal

differences in sea ice retreat and/or the advection of saline water masses in the bottom layer along the shelf. The export of shelf production beyond the shelf break regions depended on the strength of upwelling and the slope of the front at the shelf break.

The development of the spring phytoplankton bloom showed strong interannual variations due to the seasonal advance and retreat of sea ice and wind mixing events. The water column temperature in early spring controlled the coupling between the phytoplankton and zooplankton, which may ultimately control the fate of spring production in the middle shelf (Alexander and Niebauer 1981; Niebauer *et al.* 1990; Niebauer *et al.* 1995).

In conclusion, this study shows that incomplete sampling of seasonal and spatial variability hindered our ability to understand the long-term variations in primary production. During the recent study (1997-2000), the mean value of the spring primary production was about 36% of that during the PROBES studies. Since the spring primary production contributed about 41-55% to the total annual production over the shelf regions, this study may be misinterpreted to support the decrease in average seasonal primary productivity about 30-40% in the northern Bering and Chuckchi Sea, based on a decrease in $\delta^{13}C$ of whale baleen between 1966 and 1997 (Schell 2000). This study showed that low primary production during recent study compared to that during the PROBES study could have resulted from lack of production measurement during the spring phytoplankton bloom. First, the development of phytoplankton bloom showed the seasonal cycles and the spatial variation over the southeastern Bering Sea shelf. Thus, lack of production measurement during the spring phytoplankton bloom and incomplete

spatial coverage could have resulted in underestimate of annual production. Second, pre-bloom nitrate concentrations over the middle shelf and annual new production calculated from the depletion of nitrate from 1979 to 2000 imply that there was no noticeable change of production over the southeastern Bering Sea (Hunt *et al.* 2002; McRoy *et al.* 2001). So taking these into account, total primary production does not appear to have changed since the PROBES sampling. However, this does not mean that the interpretation of $\delta^{13}C$ isotope data was wrong because bowhead whales do not feed in the southeastern Bering Sea shelf frequently (Braham 1984; Schell 2000).

To better estimate of total annual primary production, this study used primary production value measured by carbon uptake rate from late March to late October. Unlike other studies of the spatial distribution of primary production in the southeastern Bering Sea (NRC 1996; Springer et al. 1996), annual primary production was similar over the inner, middle, and outer shelves and the shelf break. The different spatial distribution of annual primary production may have resulted from the better seasonal and spatial coverage in this study. However, the results of this study could not be used to verify the presence of "the Green belt" in the shelf break region because of the elevation of production of high trophic levels in the shelf break region (Springer *et al.* 1996 and references therein). Although this study included the sufficient seasonal cycle of primary production, the frequency of production measurements was not enough to allow robust estimate of primary production in the shelf break region that would be comparable to the middle and outer shelves (Table 3.1). The ecosystem dynamics in the shelf break region was poorly understood due to lack of data and that status still exists.

The lack of primary production measurements, needed for a better evaluation of the seasonal and spatial variations, hampered our ability to understand the long-term variations of primary production over the southeastern Bering Sea shelf. In order to better understand the interannual changes in primary production over the southeastern Bering Sea shelf, we need more seasonal measurements of primary production over the inner shelf and in the shelf break region including sampling of the spatial variations across and along the shelf. We also need more studies of the relationship between the strength of the front in the shelf break region, the development of the spring phytoplankton bloom, and the interaction between trophic levels occurring there.

References

Alexander, V. and H. J. Niebauer (1981). Oceanography of the eastern Bering Sea ice-edge zone in spring. Limnology and Oceanography **26**: 1111-1125.

Coachman, L. K. (1986). Circulation, water masses, and fluxes on the southeastern Bering Sea shelf. Continental Shelf Research **5**: 23-108.

Coyle, K. O. and R. T. Cooney (1988). Estimating carbon flux to pelagic grazers in the ice-edge zone of the eastern Bering Sea. Marine Biology **98**: 299-306.

Coyle, K. O. and A. I. Pinchuk (2002). Climate-related differences in zooplankton density and growth on the inner shelf of the southeastern Bering Sea. Progress in Oceanography **55**: 177-194.

Hansell, D. A., J. J. Goering, J. J. Walsh, C. P. McRoy, L. K. Coachman, and T. E. Whitledge (1989). Summer phytoplankton production and transport along the shelf break in the Bering Sea. Continental Shelf Research **9**: 1085-1104.

Hansell, D. A., T. E. Whitledge, and J. J. Goering (1993). Patterns of nitrate utilization and new production over the Bering -Chukchi shelf. Continental Shelf Research **13**: 601-627.

Hunt, G. L., Jr. (2003). The southeastern Bering Sea: Recent advances in knowledge, A synthesis of contributions from the southeastern Bering Sea carrying capacity program Bering Sea FOCI and The Inner Front Program, The SEBSCC synthesis Working Group.

Hunt, G. L., Jr. and P. J. Stabeno (2002). Climate change and the control of energy flow in the southeastern Bering Sea. Progress in Oceanography **55**: 5-22.

Kachel, N. B., G. L. Hunt, Jr., S. A. Salo, J. D. Schumacher, P. J. Stabeno, and T. E. Whitledge (2002). Characteristics and variability of the inner front of the southeastern Bering Sea. Deep-Sea Research II **49**: 5889-5909.

Kopylov, A. I., M. V. Flint, and A. V. Drits (2002). Primary production of phytoplankton in the eastern part of the Bering Sea. Oceanology **42**: 215-225.

McRoy, C. P., J. J. Goering, and W. E. Shiels (1972). Studies of primary production in the eastern Bering Sea. Biological oceanography of the northern North Pacific Ocean. A. Y. Takenouti. Tokyo, IDEMITSU SHOTEN: 199-216.

McRoy, C. P., D. W. Hood, L. K. Coachman, J. J. Walsh, and J. J. Goering (1986). Processes and resources of the Bering Sea shelf (PROBES): the development and accomplishments of the project. Continental Shelf Research **5**: 5-21.

Niebauer, H. J., V. Alexander, and S. M. Henrichs (1990). Physical and biological oceanographic interaction in the spring bloom at the Bering Sea marginal ice edge zone. Journal of Geophysical Research **95**: 22229-22241.

Niebauer, H. J., V. Alexander, and S. M. Henrichs (1995). A time-series study of the spring bloom at the Bering Sea ice edge I. Physical processes, chlorophyll and nutrient chemistry. Continental Shelf Research **15**: 1859-1877.

NRC (1996). The Bering Sea Ecosystem, National Academy Press. 324 pp.

Rho, T. K. (2000). Carbon and nitrogen uptake dynamics during 1997 and 1998 anomalous conditions in the Bering Sea. M.S. Thesis, University of Alaska Fairbanks. 95 pp.

Sambrotto, R. N., H. J. Niebauer, J. J. Goering, and R. L. Iverson (1986). Relationships among vertical mixing, nitrate uptake, and phytoplankton growth during the spring bloom in the southeast Bering Sea middle shelf. Continental Shelf Research **5**: 161-198.

Schell, D. M. (2000). Declining carrying capacity in the Bering Sea: Isotopic evidence from whale baleen. Limnology and Oceanography **45**: 459-462.

Slawyk, G., Y. Collos, and J. C. Auclair (1977). The use of the ^{13}C and ^{15}N isotopes for the simultaneous measurement of carbon and nitrogen turnover rates in marine phytoplankton. Limnology and Oceanography **22**: 925-932.

Smith, S. L. and J. Vidal (1986). Variations in the distribution, abundance, and development of copepods in the southeastern Bering Sea in 1980 and 1981. Continental Shelf Research **5**: 215-239.

Sorokin, Y. I. (1999). Data on primary production in the Bering Sea and adjacent North Pacific. Journal Plankton Research **21**: 615-636.

Springer, A. M. (1998). Is it all climate change? Why marine bird and mammal populations fluctuate in the North Pacific. Biotic impacts of extratropical climate variability in the Pacific. G. Halloway, P. Muller and D. Henderson, University of Hawaii: 109-119.

Springer, A. M., C. P. McRoy, and M. V. Flint (1996). The Bering Sea Green Belt: shelf-edge processes and ecosystem production. Fisheries Oceanography **5**: 205-223.

Stabeno, P. J., N. A. Bond, N. B. Kachel, S. A. Salo, and J. D. Schumacher (2001). On the temporal variability of the physical environment over the south-eastern Bering Sea. Fisheries Oceanography **10**: 81-98.

Stabeno, P. J., J. D. Schumacher, R. F. Davis, and J. M. Napp (1998). Under-ice observations of water column temperature, salinity and spring phytoplankton dynamics: Eastern Bering Sea shelf. Journal of Marine Research **56**: 239-255.

Whitledge, T. E., W. S. Reeburgh, and J. J. Walsh (1986). Seasonal inorganic nitrogen distributions and dynamics in the southeastern Bering Sea. Continental Shelf Research **5**: 109-132.

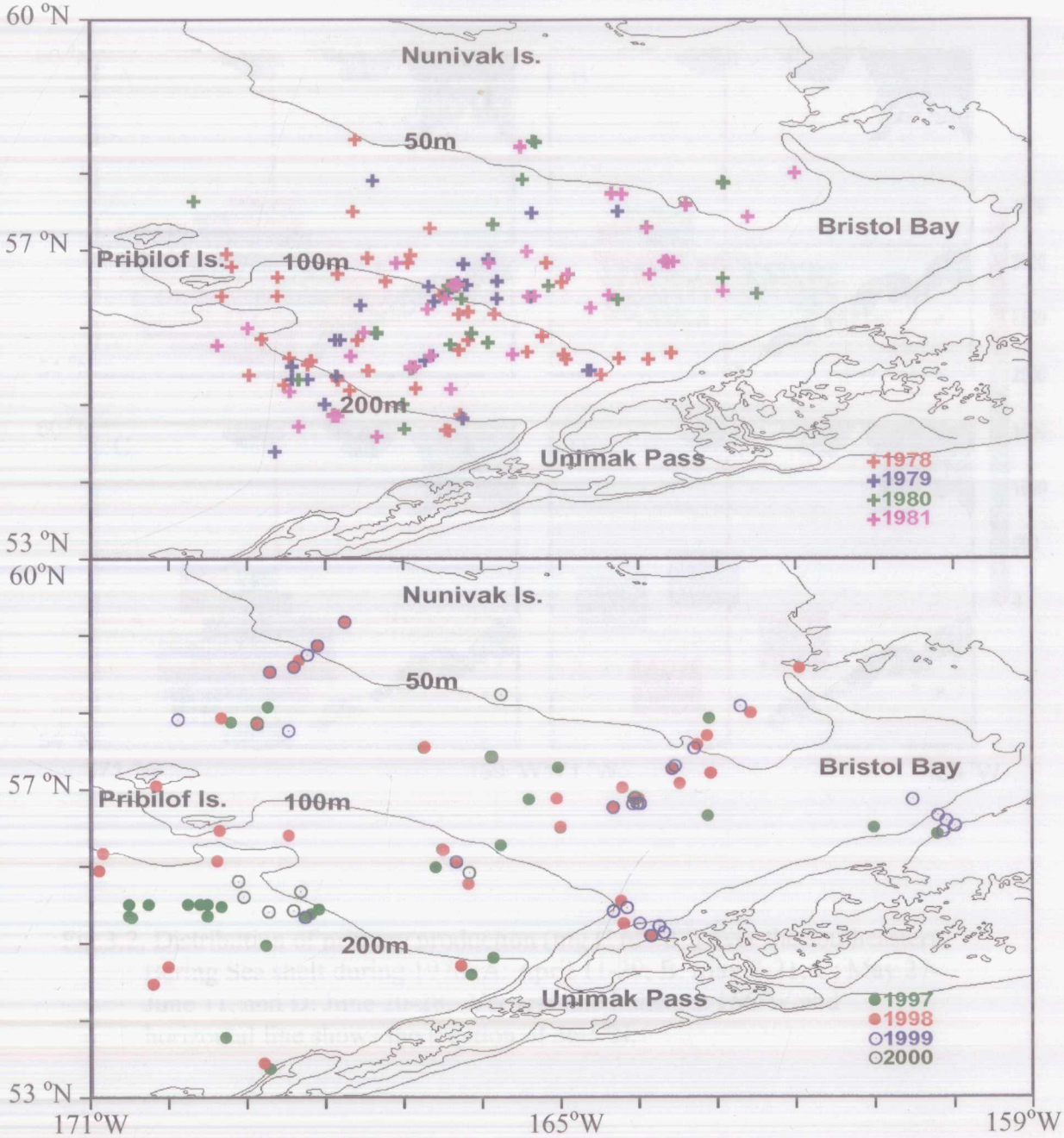

Fig. 3.1. Location of productivity stations over the southeastern Bering Sea shelf during PROBES (upper panel) and the recent measurements (lower panel)

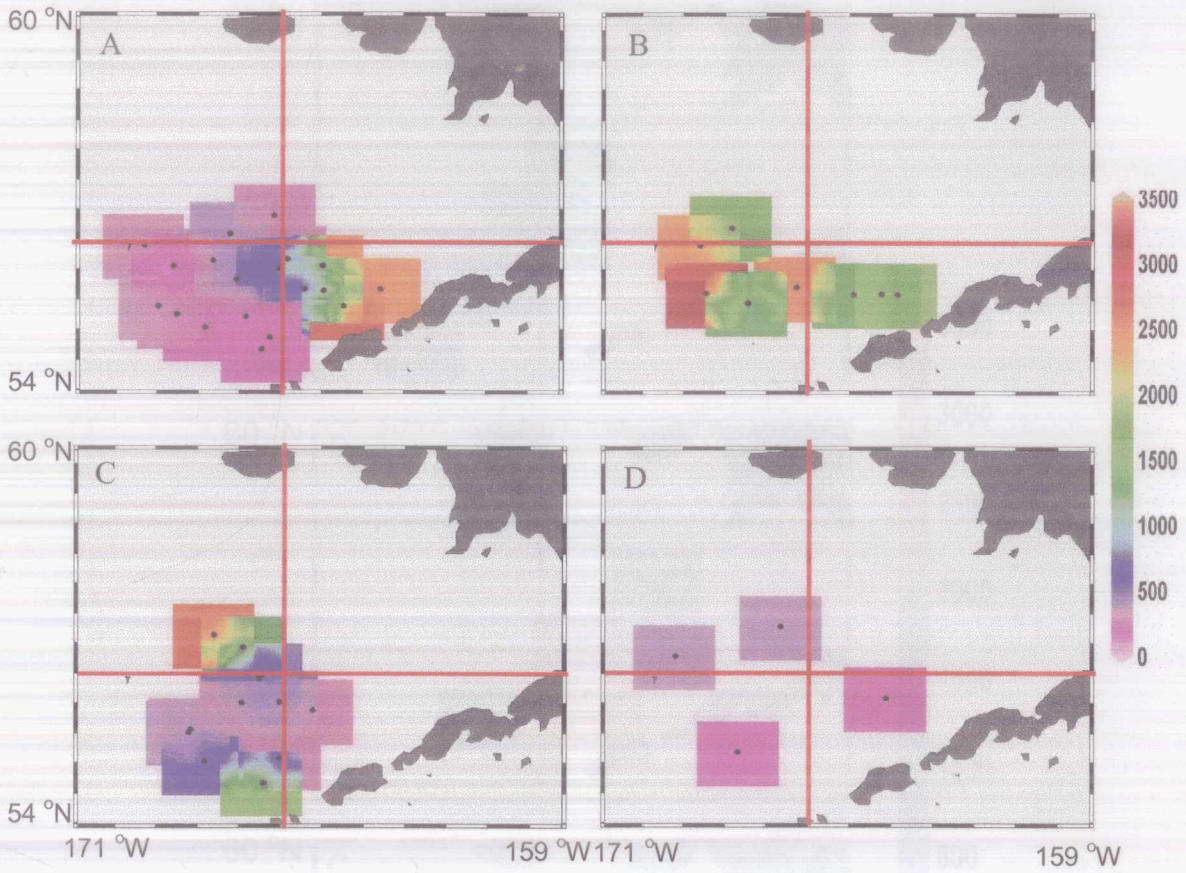

Fig.3.2. Distribution of primary production (mg C m^{-2} d^{-1}) over the southeastern Bering Sea shelf during 1978. A: April 11-29, B: May 7-21, C: May 27-June 11, and D: June 20-28. Vertical line indicates 166°W and horizontal line shows the location of 56.5°N.

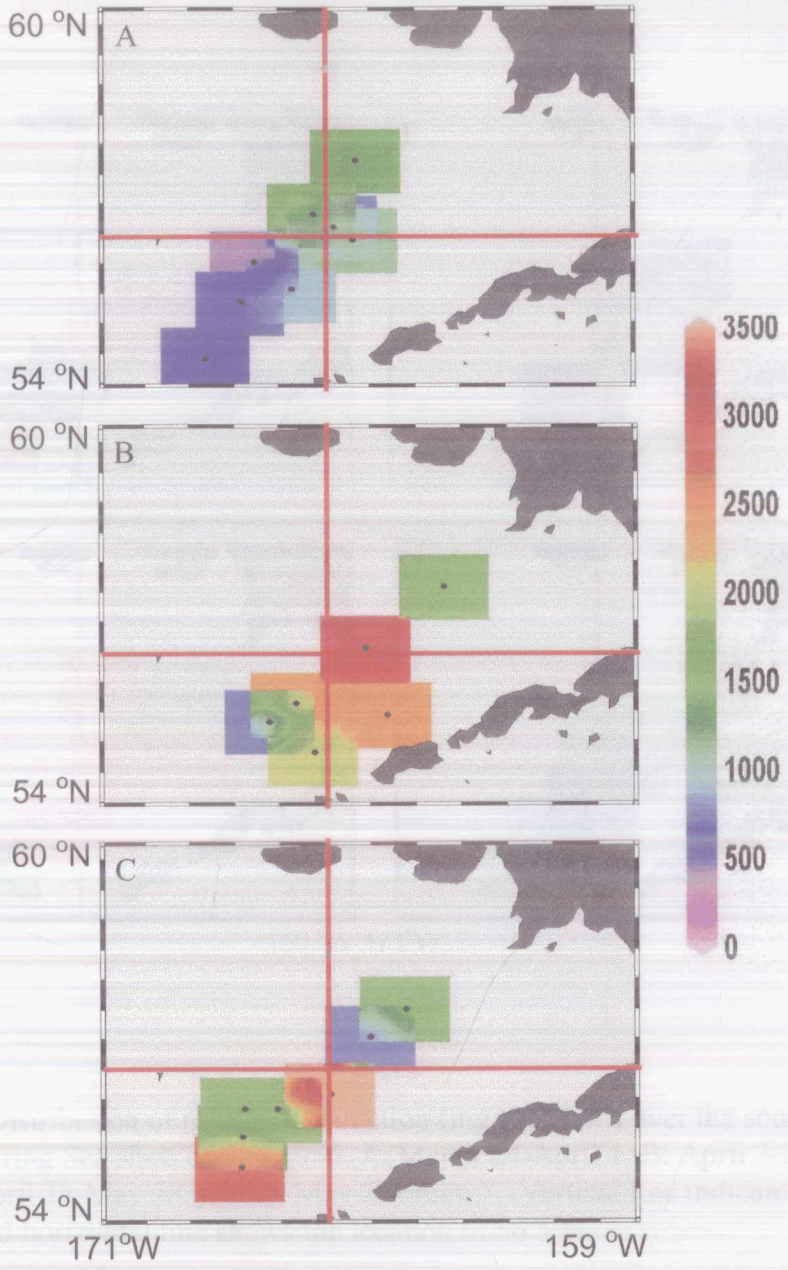

Fig.3.3. Distribution of primary production (mg C m^{-2} d^{-1}) over the southeastern Bering Sea shelf during 1979. A: April 14-25, B: May 3-20, and C: May 25-June 14. Vertical line indicates 166°W and horizontal line shows the location of 56.5°N.

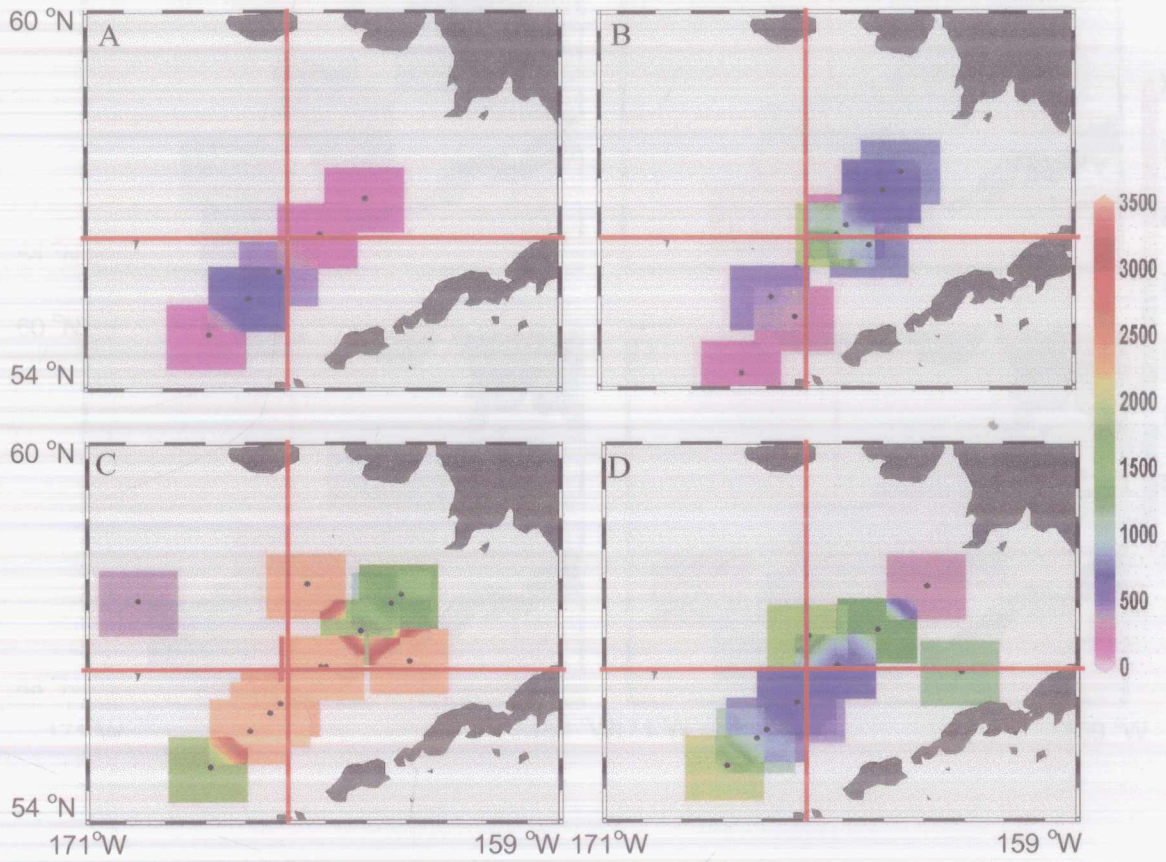

Fig.3.4. Distribution of primary production (mg C m^{-2} d^{-1}) over the southeastern Bering Sea shelf during 1980. A: March 24-April 1, B: April 7-23, C: April 28-May 18, and D: May 22- June 7. Vertical line indicates 166°W and horizontal line shows the location of 56.5°N.

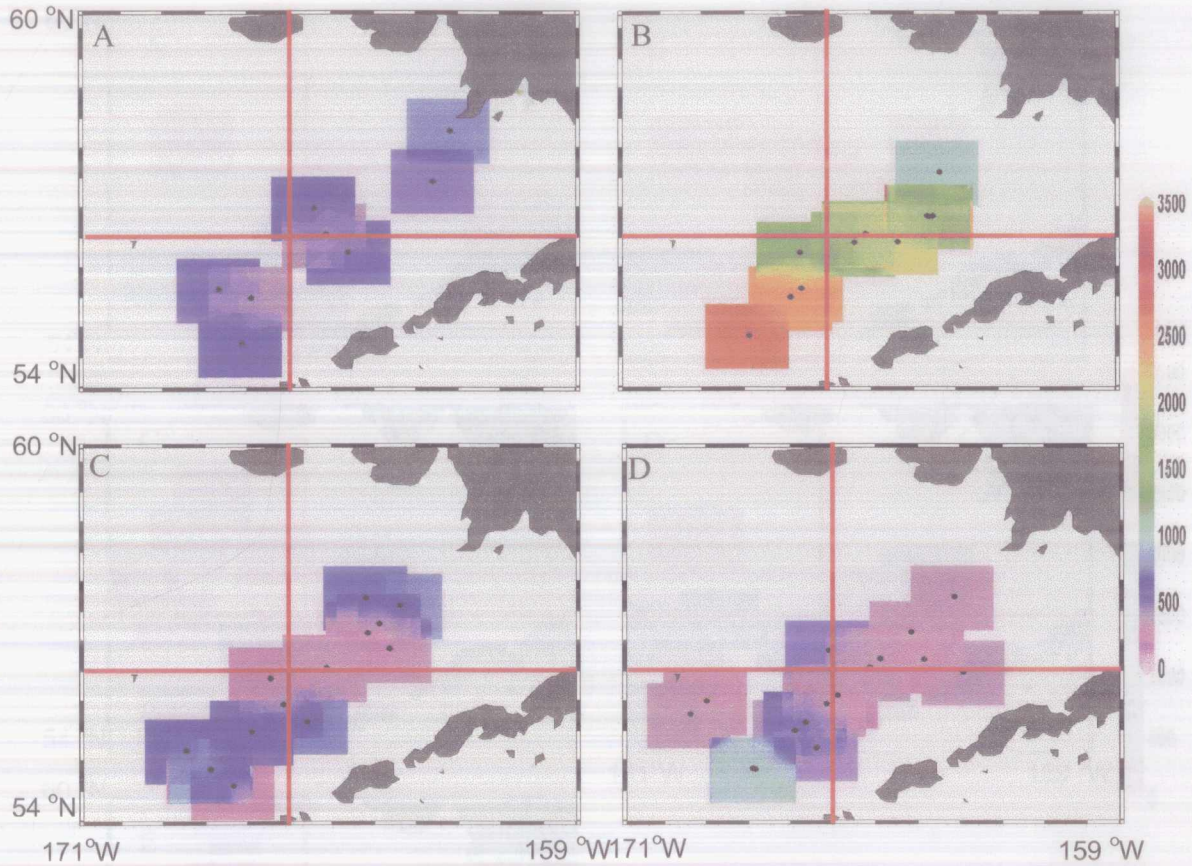

Fig.3.5. Distribution of primary production (mg C m^{-2} d^{-1}) over the southeastern Bering Sea shelf during 1981. A: April 13-April 24, B: April 30-May 25, C: June 1-June 20, and D: June 27- July 20. Vertical line indicates 166°W and horizontal line shows the location of 56.5°N.

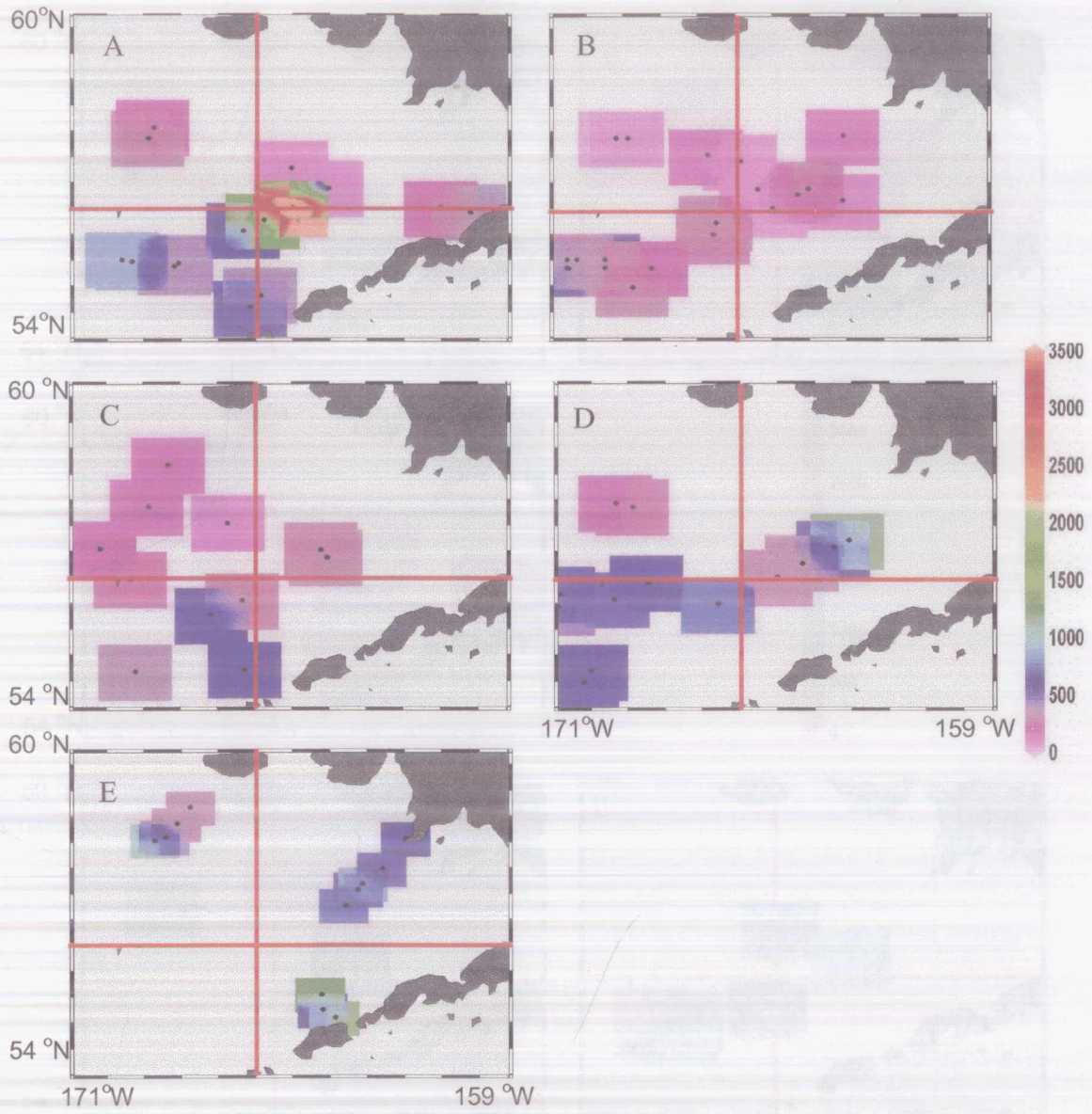

Fig.3.6. Distribution of primary production (mg C m^{-2} d^{-1}) over the southeastern Bering Sea shelf during 1997 and 1998. A: May 4-May 12 1997, B: June 11-June 25 1997, C: April 16-April 26 1998, D: May 10- 21 1998, and E: August 20- September 4 1998. Vertical line indicates 166°W and horizontal line shows the location of 56.5°N.

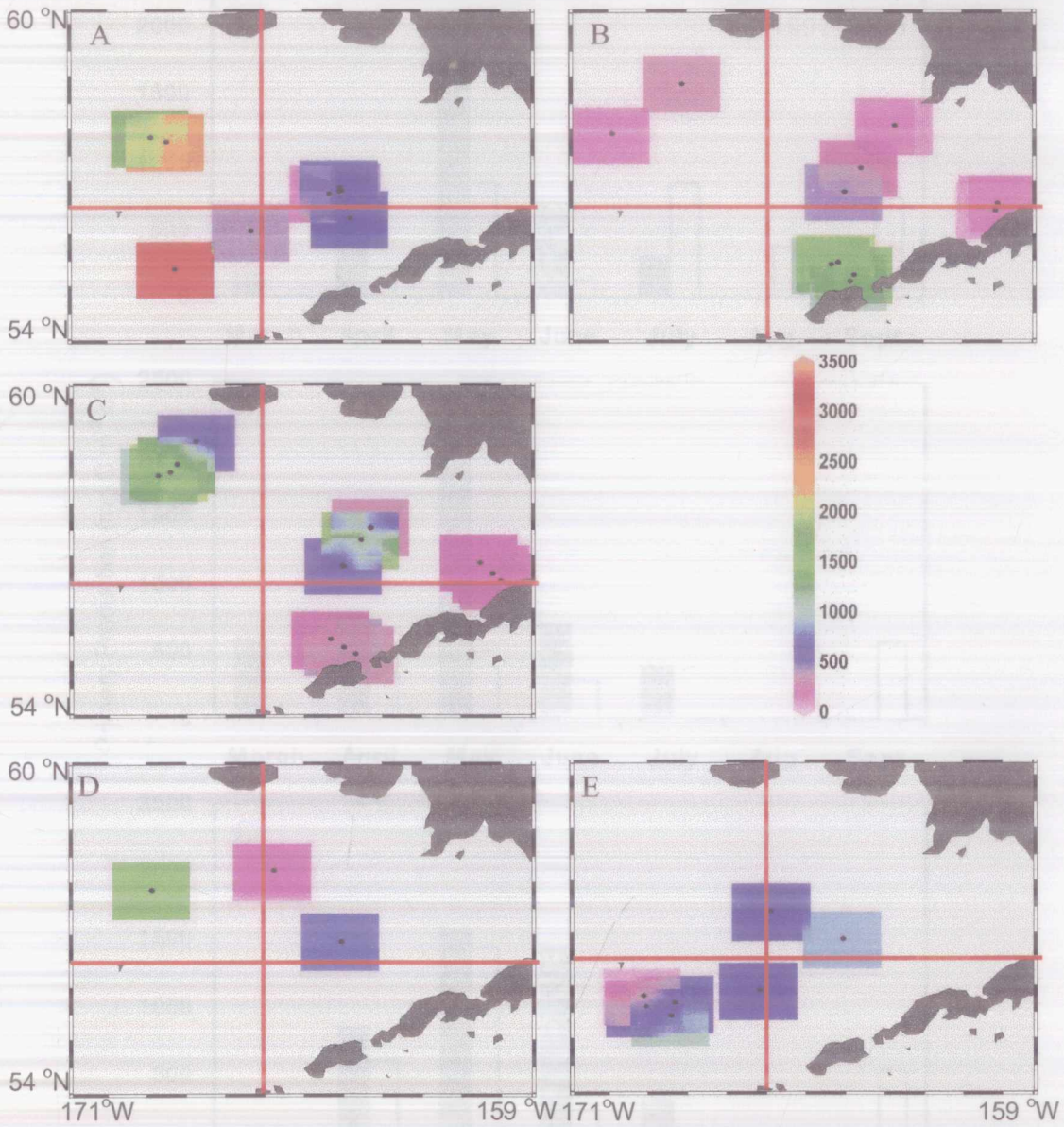

Fig.3.7. Distribution of primary production (mg C m^{-2} d^{-1}) over the southeastern Bering Sea shelf during 1999 and 2000. A: May 2-May 9 1999, B: May 20-June 11 1999, C: July 23- August 15 1999, D: June 30- July 17 2000, and E: August 31-September 8 2000. Vertical line indicates 166°W and horizontal line shows the location of 56.5°N.

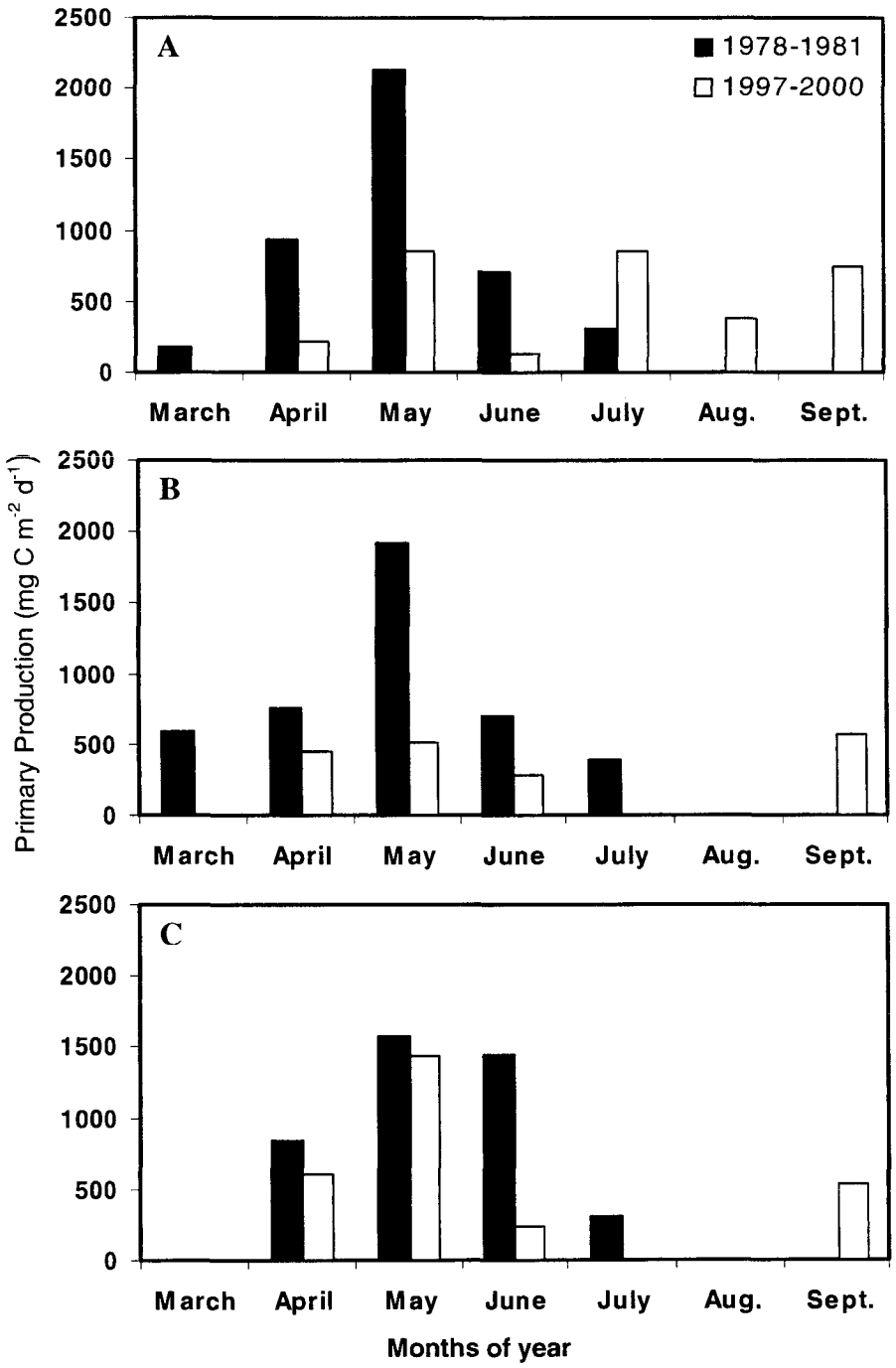

Fig.3.8. Annual cycles of primary production in the southeastern Bering Sea. (A: middle shelf, B:outer shelf, and C: shelf break). For convenience of comparison, mean primary production was calculated for a one-month period instead of for the duration of the cruise. The inner shelf was not included, due to the lack of measurements during 1978 and 1979.

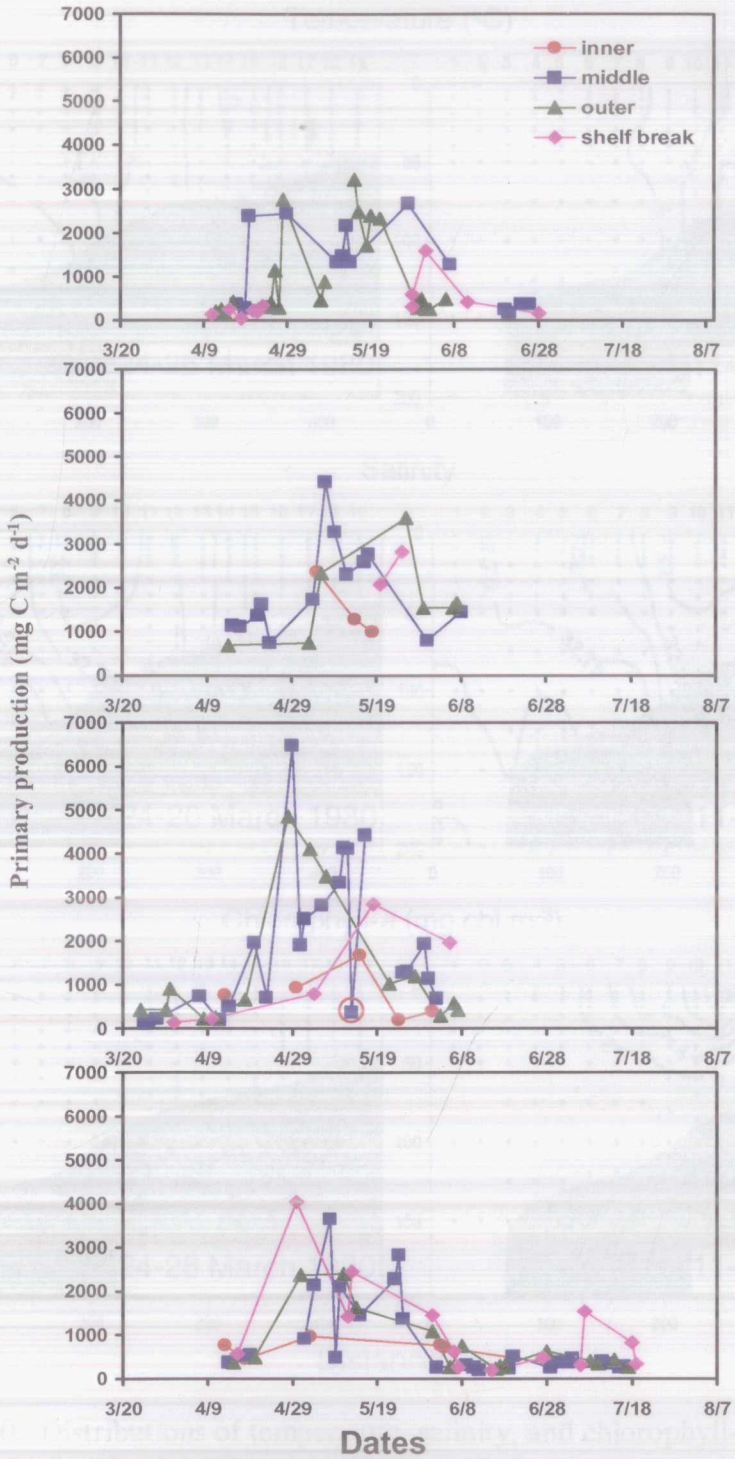

Fig.3. 9. Seasonal progression of primary production over the southeastern Bering Sea shelf (A: 1978, B: 1979, C: 1980, and D: 1981). All production measurements were plotted in each domain. The open circle in panel C indicates primary production in the northern part of the southeastern Bering Sea shelf.

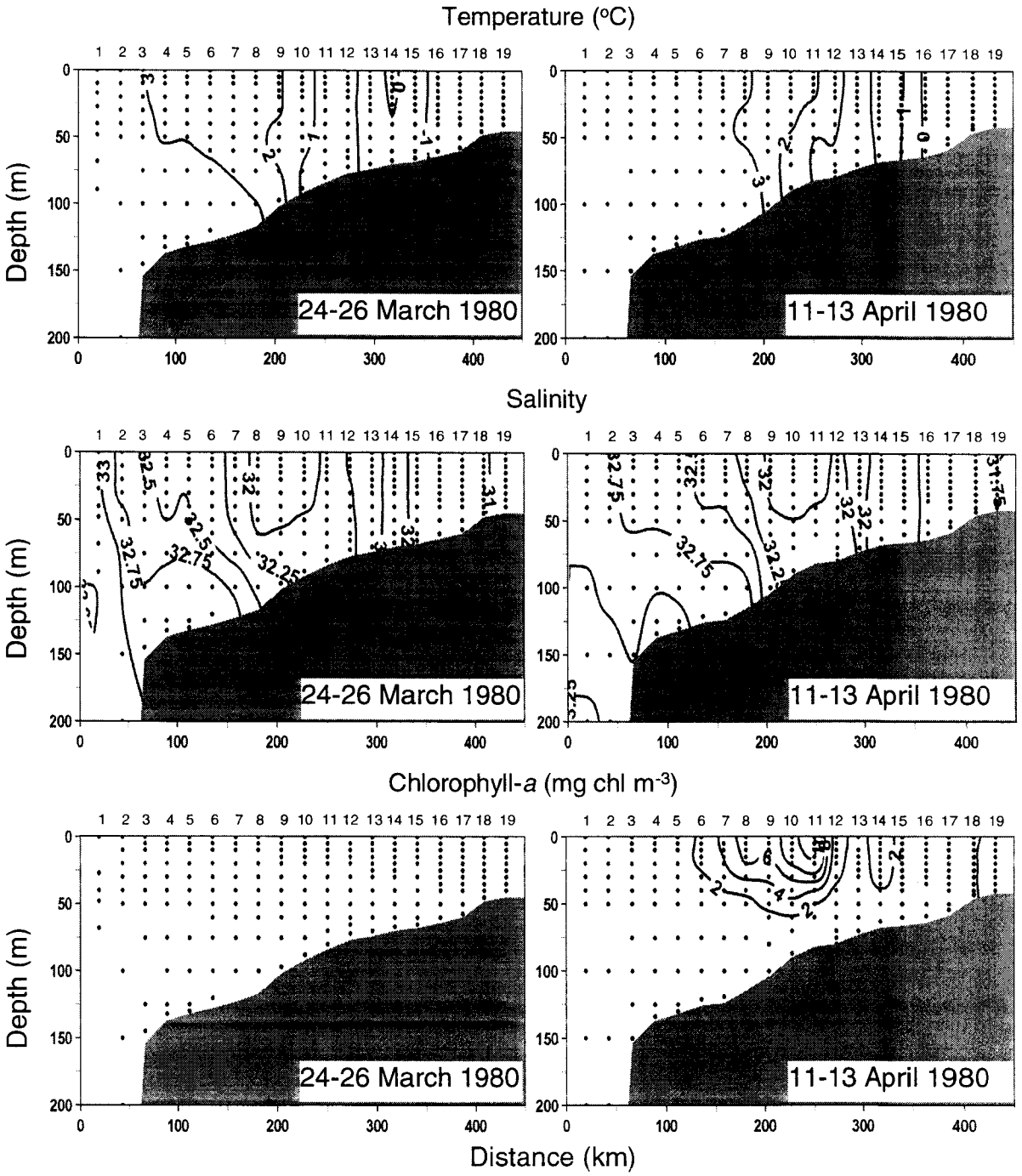

Fig.3.10. Distributions of temperature, salinity, and chlorophyll-*a* during 24-26 March 1980 and 11-13 April 1980.

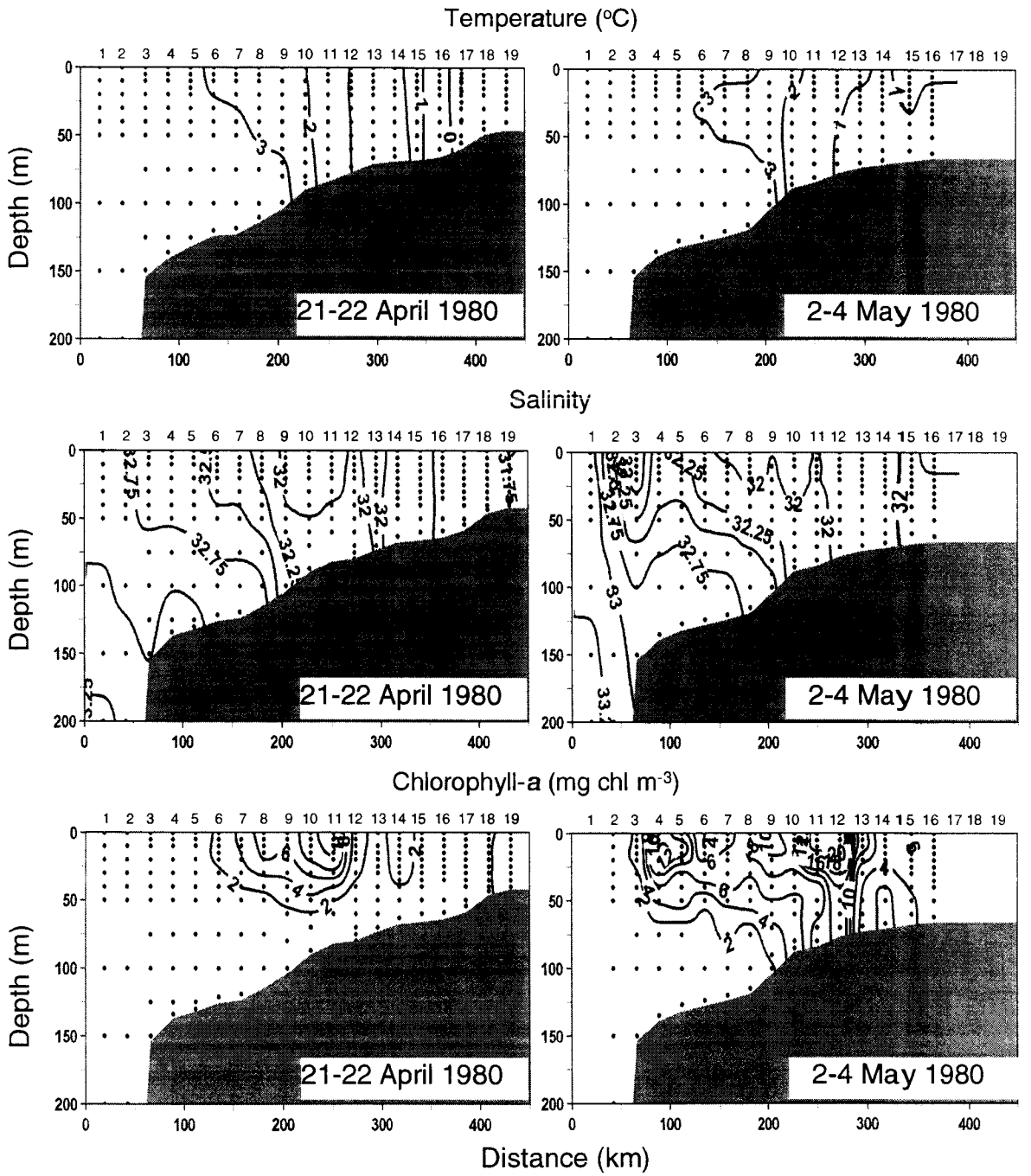

Fig.3.11. Distributions of temperature, salinity, and chlorophyll-*a* during weak front (21-23 April 1980) and strong front (2-4 May 1980) conditions.

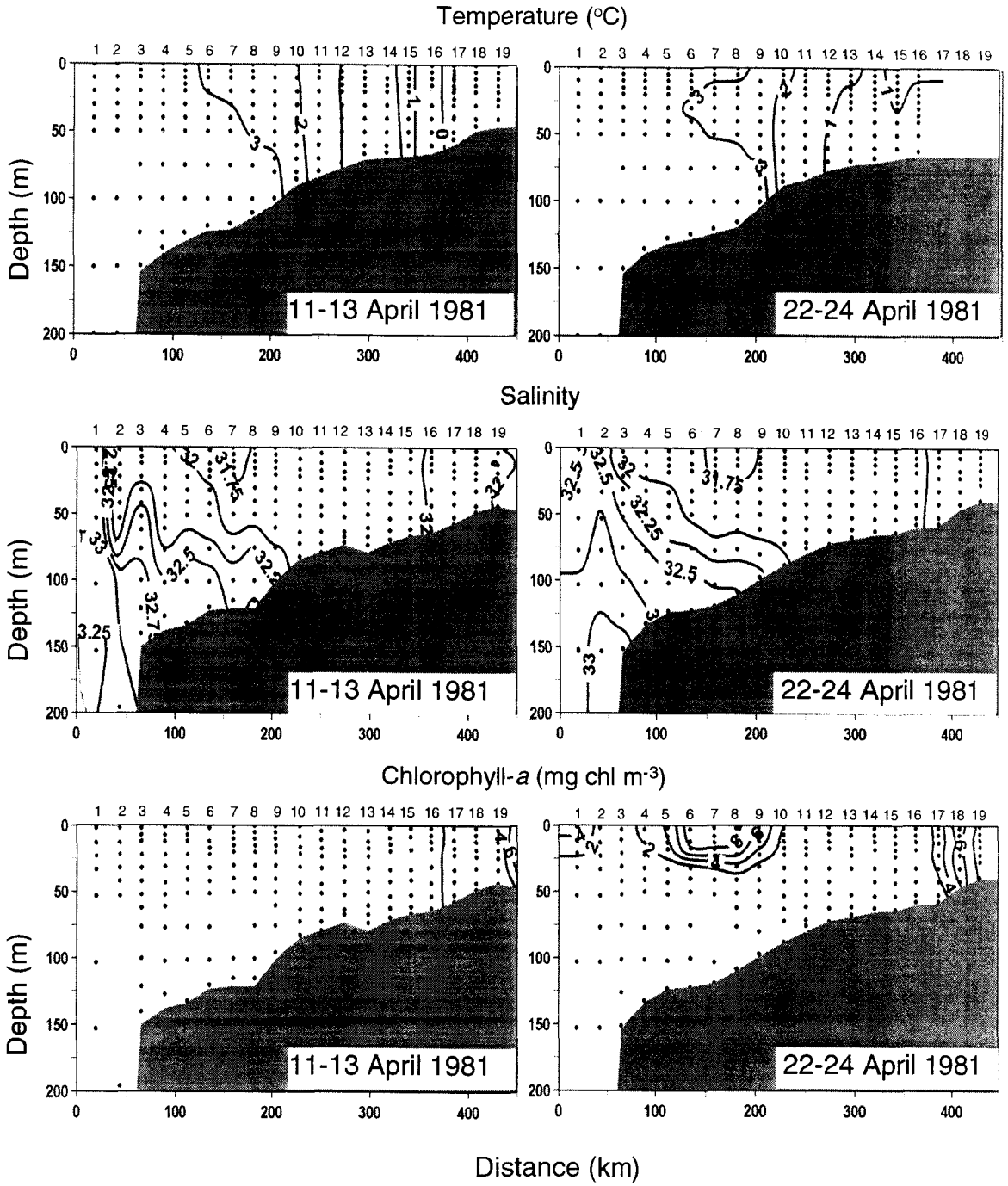

Fig.3.12. Distributions of temperature, salinity, and chlorophyll-*a* during 11-13 April 1981 and 22-24 April 1981.

Table 3.1. Mean primary production over the southeastern Bering Sea shelf (mg C m^{-2} d^{-1}). For each domain, the number of stations is indicated by n.

Year	Date	Inner shelf	n	Middle shelf	n	Outer shelf	n	Shelf break	n	Open ocean	n
1978	4/11-4/29			1375.6	4	658.2	9	204.3	6		
	5/7-5/21			1578.0	4	1921.2	7				
	5/27-6/11			1977.9	2	473.8	6	726.7	4		
	6/20-6/28			291.6	4			174.9			
1979	4/14-4/25			1203.3	5	654.0	2	684.5	1	591.2	1
	5/3-5/20	1550.1	3	2857.9	6	1727.4	3				
	5/25-6/14			1128.7	2	2084.7	4	2835.5	1		
1980	3/24-4/1			176.4	2	593.3	3	140.0	1		
	4/7-4/23	771.7	1	827.1	5	380.4	3	221.2	1		
	4/28-5/18	1316.6	2	3348.8	9	4149.3	3	1824.2	2		
	5/22-6/7	302.5	2	1266.0	5	703.4	5	1968.3	1		
	10/4-10/24	770.3	1	214.6	1	393.9	2	419.0	1		
1981	4/13-4/24	612.0	2	481.0	3	430.4	2	582.2	1		
	4/30-5/25	965.8	1	1918.3	9	2137.6	3	2648.3	3		
	6/1-6-20	736.6	2	279.9	6	490.8	6	639.3	4		
	6/27-7/20	337.3	1	346.1	8	409.2	5	704.0	5		
1997	5/4-5/12			974.4	4	601.1	1	637.1	4	526.2	1
	6/11-6/25	93.4	2	104.7	8	280.2	2	328.5	9		
1998	4/16-4/25			223.2	9	448.1	2	605.0	1	371.4	2
	5/10-5/25			467.4	8	607.8	4	521.9	3	516.2	2
	8/20-9/4	699.2	12								
1999	5/2-5/9			973.1	9	413.0	1	3284.7	1		
	5/20-6/11	709.3	9	325.3	3						
	7/23-8/15	705.1	12	493.0	2						
2000	6/30-7/17	190.3	1	1087.4	11						
	8/31-9/8			750.9	2	568.6	1	528.2	4		

Table 3.2. Annual primary production over the southeastern Bering Sea shelf (g C m^{-2}). Annual production was estimated by multiplication of mean seasonal primary production by the number of days in each season.

Periods	Days	Inner shelf	Middle shelf	Outer shelf	Shelf break	Open Ocean
Late Winter (3/24-4/1)	17	-	3.0	10.1	2.4	-
Spring - early Summer (4/11- 6/11)	61	54.3	79.8	70.7	78.6	30.6
Summer (6/12-8/30)	79	36.4	34.5	31.1	36.5	-
Fall (8/31-10/24)	55	42.4	26.6	26.5	26.0	-
Annual Production	**212**	**133.1**	**143.9**	**138.4**	**143.5**	**30.6**

Chapter 4. Factors Controlling Dynamics of Nutrients and Phytoplankton in the Southeastern Bering Sea Shelf Break Regions During the Summer of 2000

Abstract

We conducted shipboard growth experiments to understand the dynamics of nutrients and phytoplankton in the highly productive area of the southeastern Bering Sea shelf break region. The observed changes in nitrate concentration indicate the presence of limiting factors preventing the complete utilization of nutrients. Several pieces of evidence suggest that the availability of iron is sufficient to support the utilization of nitrate by phytoplankton. Chlorophyll-*a*, POC, and PON concentrations increased in the incubation bottles over time. Carbon and nitrate uptake rates also increased throughout the incubations. The small decrease in silicate concentration suggests that small phytoplankton, nonsiliceous phytoplankton and lightly silicified pennate diatoms, were dominant in the phytoplankton community. Ammonium concentrations showed little change with time, although the ammonium uptake rates increased, which suggested that the recycling of nitrogen was very efficient in our experiments. The continuous supply of ammonium by efficient remineralization and the high grazing rates of microzooplankton on small phytoplankton may have prevented the complete utilization of nitrate in our experiments. Along with the continuous supply of high nutrient water, high grazing on phytoplankton prevents complete utilization of nitrate and maintains continuously high productivity in the shelf break area.

Keywords: POC, PON, Shelf break, southeastern Bering Sea shelf, nutrient utilization,

4.1. Introduction

The southeastern Bering Sea is generally recognized as very highly productive in upper trophic levels, sustaining large populations of marine mammals, seabirds, fish, and shellfish (NRC 1996). It consists of a broad, shallow continental shelf and a deep basin, which are separated by the shelf break frontal region. Many studies have shown that high productivity in upper trophic levels is associated with the shelf break frontal zone, which is coincident with a narrow band of high chlorophyll-*a* concentrations (Iverson *et al.* 1979; Springer *et al.* 1996). High production has been found during summer in the vicinity of the shelf break front and primary production rates correspond to those of the spring bloom over the shelf areas (Springer et al. 1996). A recent study around St. Paul Island also showed that the summer values of phytoplankton numbers, biomass, and primary production in the shelf break frontal region are similar to those of the shelf region during the spring bloom (Flint *et al.* 2002).

Knowledge of physical conditions is critical to understanding productivity of the upper trophic levels in marine ecosystems. In the Bering Sea, the physical mechanisms resulting in the higher productivity in the shelf break region are partially known. The important mechanisms, which supply nutrients to the euphotic layer and enhance primary and secondary production, are intensive tidal mixing, transverse circulation, and the activity of eddies in the Bering Slope Current (Springer *et al.* 1996 and references therein). Uz *et al.* (2001) also observed the enhancement of chlorophyll-*a* concentration following a disturbance caused by planetary waves. Eddies not only provide nutrients to

the euphotic zone, but also entrain planktonic organisms, which could enhance the coupling between lower trophic levels and higher trophic levels (Springer *et al.* 1996).

Many observations have shown that chemical and biological processes are also very important in controlling nutrient utilization and growth of phytoplankton. The availability of iron controls the growth of large diatom species, and grazing by the micrograzer community prevents the complete utilization of nitrate and results in high nitrate low chlorophyll (HNLC) conditions in the surface layer of some parts of the world oceans: the equatorial Pacific, the northeast Pacific, and the Southern Ocean (Miller *et al.* 1991; Landry *et al.* 1997; Boyd *et al.* 2001). Recent research has shown that the availability of iron is also important in understanding the dynamics of nutrient utilization and growth of phytoplankton in coastal upwelling regions (Hutchins and Bruland 1998; Hutchins *et al.* 1998; Hutchins *et al.* 2002).

The dynamics of phytoplankton growth and nutrient utilization over the southeastern Bering Sea shelf were studied during the Processes and Resources of the Bering Sea Shelf (PROBES) study from 1978-1981. Physical, chemical, and biological factors were reported to play important roles in regulating the spatial and seasonal distribution of phytoplankton over the southeastern Bering Sea shelf (Goering and Iverson 1981; Sambrotto *et al.* 1986; Whitledge *et al.* 1986). In the vicinity of the shelf break front, nutrient concentrations are elevated compared to the adjacent regions, and high nutrient and chlorophyll-a concentrations occur in the surface layer during summer, leading to the nickname "the Green belt" for this area (Springer *et al.* 1996; Flint *et al.*

2002). *Phaeocystis pouchetii* constituted a large proportion of the phytoplankton communities over the outer shelf and the shelf break regions of the Bering Sea, which may be the result of preferential grazing on large plankton by macrograzers (Goering and Iverson 1981; Springer *et al.* 1996; Flint *et al.* 2002). However, the utilization of nutrients and growth of phytoplankton are poorly understood in the shelf break frontal ecosystem.

In this study, we investigated the dynamics of phytoplankton growth and nutrient uptake using shipboard incubation of surface waters from the shelf area and subsurface waters from the open ocean. We also examined the effects of mixing the two different water masses on phytoplankton growth and nutrient uptake. Our results demonstrated that the availability of iron is not the limiting factor for growth and nitrate utilization of phytoplankton in the outer shelf and shelf break regions. In addition to a continuous supply of nitrate, the intense grazing by micrograzer may prevent complete utilization of nitrate either by direct control on the population size of small phytoplankton or indirect control via the supply of ammonium to the water column. The experimental results are very important to understanding the mechanism of high productivities in the "Green belt" area.

4.2. Materials and Methods

4.2.1. Water collection and shipboard incubations

For mixing experiments using shelf water and open water, we collected surface and subsurface waters on 30 August 2000 from a shelf region (55.55 ^{o}N, 167.77 ^{o}W,

140m) and on 1 September 2000 from an open ocean region (55.12 °N, 168.60 °W, 1933m) (Fig.4.1). Sea surface temperatures and salinities at those locations were 8.79°C and 32.79 psu (shelf region) and 8.02°C and 32.88 psu (open region), respectively. The surface water from the shelf region was divided into two fractions. The large zooplankton were removed with a 333µm screen during water collection. One fraction was transferred into an acid-cleaned 10L polycarbonate incubation bottle, and the other fraction was filtered using a GF/F glass fiber filter to remove the particulate matter. 4L of filtered surface shelf water were mixed with 9L of unfiltered subsurface open water and placed the mixture in an incubation bottle. The bottles were incubated for 5 days in the onboard incubator, cooled with running surface seawater and under 100% of the ambient light level.

4.2.2. Nutrient analysis

Nutrient concentrations were measured from all water samples on board according to the methods of Whitledge *et al.* (1981), using automated continuous flow analyzers.

4.2.3. Chlorophyll-*a* analysis

Subsamples (200-300ml) for chlorophyll analysis were collected and filtered using GF/F filters. The filters were stored in a freezer until extraction of the pigments. Extraction was done overnight using an acetone/DMSO procedure (Shoaf and Lium 1976). Concentrations of chlorophyll-*a* were measured fluorometrically using a Turner Designs Model 10-005RU Fluorometer (Parsons *et al.* 1984).

4.2.4. Carbon and nitrogen uptake rates

Subsamples for carbon and nitrogen uptake rate measurements were collected and transferred to polycarbonate bottles (300ml), which were inoculated according to a double labeling technique (Slawyk *et al.* 1977). The bottles were incubated on-deck and cooled with circulating surface seawater. After 4 hr, the incubations were terminated by filtering the water onto precombusted (at 450° C for 4hr) GF/F filters. The filters were frozen until analyzed in the Fairbanks laboratory.

4.2.5. POC, PON, and isotope analysis

In the laboratory, the samples were fumed with hydrochloric acid to remove inorganic carbon from the filters, and subsequently dried at 60° C for 24 hr. The isotope ratios and POC and PON concentrations of the samples were determined using a Finigan Delta+XL IRMS. The equation of Dugdale and Goering (1967) was utilized to calculate carbon and nitrogen uptake rates. The isotopic dilution effect was not included in our uptake calculation because we used a short-term incubation (Glibert *et al.* 1982).

4.3. Results

4.3.1. Nutrients

Nutrient concentrations, except ammonium, declined in all treatments (Fig.4.2). Nitrate concentrations decreased generally in all treatments, and nitrate consumption rates were slightly higher after day 3. Phytoplankton did not utilize nitrate completely until day 5 in all treatments. Total nitrate consumption during the experiments was 4.3, 8.1, and 11.7 $\mu mol\ l^{-1}$ in the shelf water, the mixed water, and the open ocean water,

respectively. The amounts of nitrate utilization were related to the initial nitrate concentration.

Silicate concentrations showed little change until day 3, and decreased only slightly after day 3 in the mixed water and the open ocean water (Fig.4.2). However, there was no net decrease of silicate concentration in the shelf water. Total silicate utilization during the experiments was 3.4 μmol l^{-1} and 5.6 μmol l^{-1} in the mixed water and the open ocean water, respectively.

Phosphate concentrations also remained almost the same as the initial values in the shelf water and the mixed water, but small decreases occurred in the open ocean water (Fig.4.2). The amounts of phosphate consumed during the experiments were 0.7 μmol l^{-1}, 1.1 μmol l^{-1}, and 0.9 μmol l^{-1} in the shelf water, the mixed water, and the open ocean water, respectively.

Ammonium concentrations slightly increased until day 2 in all experiments, and then, maintained the same concentrations during the remainder of the experiments in the mixed water and the open ocean water (Fig.4.2). In the shelf water, ammonium concentrations decreased slightly and then maintained the same concentration after day 3.

4.3.2. Chlorophyll-*a* concentrations

Chlorophyll-*a* concentrations increased in all experiments (Fig.4.3). Final chlorophyll-*a* concentrations were about 3-7 times greater than the initial value. In the mixed and open ocean waters, the chlorophyll-*a* concentrations were about two times

higher than in the shelf water on day 5. There was a large difference between the measured concentration and the concentration estimated based on the chlorophyll-*a* concentration of open ocean water using the dilution factor.

Chlorophyll-*a* specific growth rates were estimated using the net chlorophyll-*a* increase, obtained by subtracting the initial from the final concentrations, which were 0.252 d^{-1}, 0.656 d^{-1}, and 0.656 d^{-1} in the shelf water, the mixed water, and the open ocean water, respectively (Table 4.1). The chlorophyll-*a* specific growth rates in the mixed water and the open ocean water were the same, but they were 2.6 times greater than those in the shelf water (Table 4.1). Chlorophyll-*a* concentrations showed little change until day 3 and then increased markedly after day 3. Therefore, actual chlorophyll-a specific growth rates would be higher if we considered the actual growing period as two days.

4.3.3. POC concentrations

POC concentrations increased 2-2.5 times in all treatments (Fig.4.4). In the shelf water, POC concentration increased from 182μg C l^{-1} to 415μg C l^{-1}. The mean rate of increase was 46.5μg C l^{-1} d^{-1} during the experiment. In the mixed water, POC concentration increased from 220μg C l^{-1} d^{-1} to 595μg C l^{-1}. The mean increase rate was 79.5μg C l^{-1} d^{-1}. In the open ocean water, POC concentration increased from 176μg C l^{-1} to 574μg C l^{-1}. The mean rate of increase was 75.0μg C l^{-1} d^{-1}. The highest POC increase rate was observed in the mixed water. The measured POC concentrations exceeded the concentrations estimated from the open ocean POC values using the dilution factor.

4.3.4. PON concentrations

PON concentrations increased 3-5 times in all experiments (Fig.4.4). In the shelf water, PON concentrations increased from 35.8μg N l^{-1} to 69.4μg N l^{-1} and the mean increase rate was 6.7μg N l^{-1} d^{-1}. In the mixed water, PON concentration increased from 20.2μg N l^{-1} to 86.6μg N l^{-1}, and the mean increase rate was 16.1μg N l^{-1} d^{-1}. In the open ocean water, PON concentrations increased from 28.2μg N l^{-1} to 108.9μg N l^{-1} and the mean increase rate was 12.3μg N l^{-1} d^{-1}. The PON concentration change estimated for the open ocean water sample was from 19.2μg N $l^{-1}$to 75.4μg N l^{-1}, and the mean rate of increase was 11.2μg N l^{-1} d^{-1}. The highest PON increase rate was also observed in the mixed water.

Initial C: N ratios of particulate matter were high (ca. 9-10) in the mixed and the open ocean water and decreased slightly (ca. 8-9) over time. In the shelf water, initial C: N ratios of particulate matter were low (ca.6) and increased to ca.8 after day 1, remaining at similar values throughout the rest of the experiment (Fig.4.5).

4.3.5. Carbon and nitrogen uptake rates

^{13}C uptake rates gradually increased with time in all experiments (Fig.4.6). Carbon uptake rates increased from 3.3 to 9.3μg C l^{-1} h^{-1}, from 0.8 to 16.9μg C l^{-1} h^{-1}, and from 1.5 to 21.3μg C l^{-1} h^{-1} in the shelf water, the mixed water, and the open ocean water, respectively. Mean uptake rates were 5.7, 6.7, and 7.9μg C l^{-1} h^{-1} in the shelf, the mixed, and the open ocean waters, respectively. Carbon specific uptake rates greatly increased

over time in the mixed and the open ocean waters, but showed little change in the shelf water.

$^{15}N\text{-}NO_3^-$ uptake rates showed trends similar to those observed in the ^{13}C uptake rates (Fig.4.7). $^{15}N\text{-}NO_3^-$ uptake rates increased from 0.06 to 0.82μg N l^{-1} h^{-1}, from 0.03 to 1.55μg N l^{-1} h^{-1}, and from 0.06 to 2.22μg N l^{-1} h^{-1} in the shelf water, the mixed water, and the open water, respectively. In the shelf water, nitrate specific uptake rates showed slight changes until day 2 and showed relatively large increases after day 3. In the mixed water, nitrate specific uptake rates showed a slight change until day 2 and increased rapidly until day 4, then increased slightly on day 5. In the open ocean water, nitrate specific uptake rates increased gradually until day 4, reached a maximum value, and remained near that value on day 5. The highest nitrate uptake rate was observed in the open ocean water, where the initial nitrate concentration was high.

$^{15}N\text{-}NH_4^+$ uptake rates showed different trends from nitrate and carbon uptake rates (Fig.4.8). Ammonium uptake rates increased from 0.65 to 3.32μg N l^{-1} h^{-1}, from 0.20 to 4.51μg N l^{-1} h^{-1}, and from 0.46 to 3.62μg N l^{-1} h^{-1} in the shelf water, the mixed water, and the open ocean water, respectively. Ammonium uptake rates gradually increased and reached a maximum value on day 5 in both the shelf and the open ocean water. In the mixed water, ammonium uptake rates slowly increased until day 2 and showed a rapid increase between day 3 and day 4.

Ammonium specific uptake rates gradually increased until day 3 and remained steady thereafter in the shelf water (Fig.4.8). In the mixed water, ammonium specific uptake rates increased rapidly after day 2 and reached a maximum rate on day 4, but they decreased on day 5. In the open ocean water, ammonium specific uptake rates reached a maximum value on day 3 and then gradually decreased as nitrate concentration rapidly decreased (Fig.4.2).

4.3.6. Nutrient biochemistry

Si: Chl-*a* ratios were 1.04 and 1.71 in the mixed water and the open ocean water, respectively (Table 4.1). The Si: Chl-*a* ratio were ca.70% higher in the open ocean water compared to the mixed water. Si: $NO3^-$ consumption ratios were 0.42 and 0.48 in the mixed water and the open water, respectively (Table 4.1). These values were low compared to those of most species of diatoms grown under Fe-replete conditions (Brzezinski 1985). A difference in the phytoplankton species composition may be responsible for the low Si: N uptake rates as observed in the Peru upwelling region (Hutchins *et al.* 2002). Nitrate: Phosphate consumption rates were 55.1, 64.5, and 24.3 in the shelf water, the mixed water and the open ocean water, respectively (Table 4.1). These ratios are very high compared to the Redfield ratio and other studies of plankton composition (Hutchins and Bruland 1998; Takeda 1998).

4.4. Discussion

It is generally recognized that the availability of nitrate limits the growth of phytoplankton in many ocean areas, but lack of iron also plays a very important role in

the utilization of nutrients in the surface layer of open ocean areas remote from land and some coastal upwelling regions (Miller *et al.* 1991; Landry, Barber *et al.* 1997; Hutchins and Bruland 1998; Hutchins *et al.* 1998; Hutchins *et al.* 2002). Extremely low levels of iron generally limit the growth of large phytoplankton, and microzooplankton graze effectively on small phytoplankton, keeping their biomass and nutrient uptake rates low, resulting in high nitrate concentrations in the surface layer of the HNLC regions (Landry *et al.* 1997; Miller *et al.* 1991). Experimental results from the late summer of 2000 suggest that the growth of phytoplankton over the shelf break region is not limited by the availability of iron. The inference from that evidence is that grazing by macro- and micro-zooplankton plays a critical role in the extent of utilization of nutrients and the dynamics of phytoplankton in the vicinity of the shelf break front.

Shipboard incubation experiments in HNLC regions have shown that incomplete utilization of nitrate occurs in control incubations with no additions, but nitrate concentrations decrease to the detection limit in iron addition bottles, in regions where iron is limiting the growth of large phytoplankton (Price *et al.* 1994; Boyd *et al.* 1996). Recent iron addition studies in the coastal upwelling area off California, which is generally considered an iron replete-region, showed varying nutrient utilization in the control bottles due to the different levels of iron availability in the surface layer (Hutchins *et al.* 1998). Our results demonstrated that phytoplankton did not completely utilize nutrients during the 5-day of incubation, which is very similar to the result that was observed in the HNLC regions, where the availability of iron limited the growth of large phytoplankton in the surface water (Fig.4.2).

However, chlorophyll-*a*, POC, and PON concentrations increased in the shelf, the mixed, and the open ocean waters without additions of iron (Fig.4.3; Fig.4.4). The increase followed the same order as the initial nitrate inventory in the incubation bottles: the open ocean water > the mixed water > the shelf water (Fig.4.2). These results differ somewhat from those of studies conducted in the HNLC regions, where the biomass of phytoplankton remained constant or showed little change in low iron concentration regions, but increased greatly when iron limitation was reduced (Price *et al.* 1994; Boyd *et al.* 1996; Hutchins *et al.* 2001). In the California coastal upwelling region, chlorophyll-*a* and POC concentrations increased in both the control and the iron addition bottles, and there was no apparent difference between the control and the iron addition bottle when iron was replete (Hutchins *et al.* 1998).

Carbon and nitrogen specific uptake rates also increased over time in all treatments (Fig.4.6; Fig.4.7; Fig.4.8). The increase of carbon and nitrogen specific rates showed a trend similar to those of chlorophyll-*a*, POC, and PON concentrations. The largest increases occurred in the open ocean water, where nutrient concentrations were the highest among the three water types studied. Other studies, conducted in HNLC regions, showed that carbon uptake rates generally increased in both the control and the iron addition bottles. However, nitrogen uptake rates showed large differences between the control and the iron addition bottles. Nitrate uptake rates of large phytoplankton showed large increases in iron addition bottles, but ammonium uptake rates showed little change (Price *et al.* 1994; Boyd *et al.* 1996). Our data showed a continuous utilization of nitrate and a gradual increase of nitrate uptake rates over time in all treatments, which

suggests that phytoplankton were growing in iron replete conditions. This is similar to the iron addition bottles in the HNLC regions. However, definitive evidence that iron is not limiting in this region will require experiments that directly compare results of iron addition to those in control bottles.

If the utilization of nitrate was not controlled by the availability of iron, there must be other factors that restrict the consumption of nitrate in our experiments. It has been reported that ambient ammonium inhibits nitrate uptake of phytoplankton in the North Pacific and the equatorial Pacific, where ammonium concentrations are greater than 1 μM (Wheeler and Kokkinakis 1990). Wheeler and Kokkinakis (1990) suggested that nitrate uptake rates were completely inhibited when ammonium concentrations were greater than 0.3 μM. In our study, ambient ammonium concentrations remained at concentrations close to 2 μM in all treatments over the entire experiment period. The high ammonium concentrations may have inhibited the utilization of nitrate. However, in our experiments, nitrate uptake rates increased continuously during the incubation, which indicates the lack of ammonium inhibition. The nitrate specific uptake rates reached steady state after day 3 in the shelf water and day 4 in the mixed and open ocean waters, although nitrate concentrations were high (shelf water: > 5 μM NO_3^-; mixed and open waters: > 10 μM NO_3^-). This suggests that individual phytoplankton, as observed via the nitrate specific uptake rates, experienced the effects of high ammonium concentration. However, the gross utilization of nitrate increased as the biomass of phytoplankton increased, as observed via the chlorophyll-*a*, POC, and PON concentration increases.

The concentrations of ammonium are controlled by the balance between production and consumption within an ecosystem. When the consumption of ammonium exceeds the production, ammonium concentrations will decrease, and the opposite also occurs. The sources of ammonium are decomposition of particulate organic materials and excretion from zooplankton. Phytoplankton utilize ammonium during photosynthesis. Although ammonium uptake rates increased over time, ammonium remained at high concentrations throughout the experiments (Fig.4.2; Fig.4.8). This suggests that large amounts of ammonium were produced to support the increase of ammonium specific uptake rates without a decrease in ammonium concentrations.

Large proportions of assimilated nitrate are converted to regenerated forms of nitrogen such as ammonium and dissolved organic nitrogen (Hutchins *et al.* 2001). The $\Delta PON/\Delta NO_3$ ratios were 0.56, 0.54, and 0.49 in the shelf, mixed, and open ocean waters, respectively. This suggests that half of the assimilated nitrate was recycled during the experiments. The small change of phosphate concentrations over time also supported the occurrence of an active recycling process in all experiments.

Large zooplankton were excluded during water collection as described in the Methods section. So, the effect of large zooplankton in the recycling of newly synthesized organic material was probably negligible in our experiments. However, microzooplankton grazing on small phytoplankton may be responsible for the active recycling of PON in our experiments. In HNLC regions, microzooplankton effectively graze small phytoplankton, and result in high concentrations of unutilized nitrate in the

surface layer (Miller *et al.* 1991). Our results showed that the increases of chlorophyll-*a*, POC and PON are greater in the mixed water than the values calculated for the mixture of open ocean water combined with filtered shelf water. The dilution with filtered seawater could have reduced the grazing by micrograzers in the mixed water compared to the open ocean water during the initial stage of growth (Fig.4.3; Fig.4.4).

Unfortunately, we did not determine the species composition of phytoplankton in our experiments. But several results suggest that the dominant organisms in our experiment may have been small nonsiliceous phytoplankton such as *Phaeocystis* and small, lightly silicified pennate diatoms, which may have been responsible for the consumption of most of the nitrogen in our experiments. Silicate concentrations remained constant or slightly decreased during our experiments (Fig.4.2) and very low Si: $NO3^-$ consumption ratios were observed (Table 4.1). Very low Si: NO_3^- utilization ratios were also observed in the subantarctic Southern Ocean (Hutchins *et al.* 2001) and offshore Humboldt Current and Peru Upwelling region (Hutchins *et al.* 2002), where nonsiliceous taxa and nanoplanktonic pennate diatoms also dominated the community. It is also known that small phytoplankton can dominate biomass in the surface water of the shelf-break and the outer shelf, due to the selective grazing on large phytoplankton by large zooplankton (Goering and Iverson 1981).

In conclusion, our results suggest that the growth of phytoplankton was not limited by the availability of iron in the outer shelf and shelf break regions. High ammonium concentrations could have inhibited the consumption of nitrate. Initially high

ammonium concentrations and the maintenance of high ammonium concentrations over time suggested that the recycling of organic material was occurring actively in our experiments. Our results suggest that microzooplankton activities played a very important role in recycling of newly produced organic material. In addition to ammonium inhibition, microzooplankton grazing intensively on small phytoplankton may have resulted in the incomplete utilization of nitrate in our experiments.

References

Banse, K. and D. C. English (1999). Comparing phytoplankton seasonality in the eastern and western subarctic Pacific and the western Bering Sea. Progress in Oceanography **43**: 235-288.

Boyd, P. W., D. L. Muggli, D. E. Varela, R. H. Goldblatt, R. Chretien, K. J. Orians, and P. J. Harrison (1996). *In vitro* iron enrichment experiments in the NE subarctic Pacific. Marine Ecology Progress Series **136**: 179-193.

Brzezinski, M. A. (1985). The Si:C:N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. Journal of Phycology **21**: 347-357.

Coachman, L. K. (1986). Circulation, water masses, and fluxes on the southeastern Bering Sea shelf. Continental Shelf Research **5**: 23-108.

Dugdale, R. C. and J. J. Goering (1967). Uptake of new and regenerated forms of nitrogen in primary productivity. Limnology and Oceanography **12**: 196-206.

Fujishima, Y., K. Ueda, M. Maruo, E. Nagayama, C. Tokutome, H. Hasegawa, M. Matsui,and Y. Sohrin (2001). Distribution of trace bioelements in the subarctic North Pacific Ocean and the Bering Sea (the R/V Hakuho Maru Cruise KH-97-2). Journal of Oceanography **57**: 261-273.

Glibert, P. M., J. J. Lipschultz, J. J. McCarthy, and M. A. Altabet (1982). Isotope dilution models of uptake and remineralization of ammonium by uptake and remineralization of ammonium by marine plankton. Limnology and Oceanography **27**: 639-650.

Goering, J. J. and R. L. Iverson (1981). Phytoplankton distribution on the southeastern Bering Sea shelf. The eastern Bering Sea shelf: oceanography and resources. Hood, D. W. and J. A. Calder (eds.). Vol.2, Seattle, University of Washington Press. **:** 933-945.

Hutchins, D. A. and K. W. Bruland (1998). Iron-limited diatom growth and Si: N uptake ratios in a coastal upwelling regime. Nature **393**: 561-564.

Hutchins, D. A., G. R. DiTullio, and K. W. Bruland (1993). Iron and regenerated production: Evidence for biological iron recycling in two marine environments. Limnology and Oceanography **38**: 1242-1255.

Hutchins, D. A., G. R. DiTullio, Y. Zhang, and K. W. Bruland (1998). An iron limitation mosaic in the California upwelling regime. Limnology and Oceanography **43**: 1037-1054.

Hutchins, D. A., C. E. Hare, R. S. Weaver, Y. Zhang, G. F. Firme, G. R. DiTullio, M. B. Alm, B. F. Riseman, J. M. Maucher, M. E. Geesey, C. G. Trick, G. J. Smith, E. L. Rue, J. Conn, and K. W. Bruland (2002). Phytoplankton iron limitation in the

Humboldt Current and Peru Upwelling. Limnology and Oceanography **47**: 997-1011.

Hutchins, D. A., P. N. Sedwick, G. R. DiTullio, P. W. Boyd, B. Quéguiner, F. B. Griffiths, and C. Crossley (2001). Control of phytoplankton growth by iron and silicic acid availability in the subantarctic Southern Ocean: Experimental results from the SAZ Project. Journal of Geophysical Research **106**: 31,559-31,572.

Koike, I., H. Ogawa, T. Nagata, R. Fukuda, and H. Fukuda (2001). Silicate to nitrate ratio of the upper sub-arctic Pacific and the Bering Sea basin in summer: Its implication for phytoplankton dynamics. Journal of Oceanography **57**: 253-260.

Landry, M. R., R. T. Barber, R. Bidigare, F. Chai, K. H. Coale, H. G. Dam, M. R. Lewis, S. T. Lindley, J. J. McCarthy, M. R. Roman, D. K. Stoecker, P. G. Verity, and J. R. White (1997). Iron and grazing constraints on primary production in the central equatorial Pacific: An EqPac synthesis. Limnology and Oceanography **42**: 405-418.

Miller, C. B., B. W. Frost, P. A. Wheeler, M. R. Landry, N. Welschmeyer, and T. M. Powell (1991). Ecological dynamics in the subarctic Pacific, a possibly iron-limited ecosystem. Limnology and Oceanography **36**: 1600-1615.

NRC (1996). The Bering Sea Ecosystem, National Academy Press: 324 pp.

Parsons, T. R., Y. Maita, and C. M. Lalli (1984). A manual of chemical and biological methods for seawater analysis, Pergamon Press. 173 pp.

Price, N. M., B. A. Ahner, and M. M. Morel (1994). The equatorial Pacific Ocean: Grazer-controlled phytoplankton populations in an iron-limited ecosystem. Limnology and Oceanography **39**: 520-534.

Sambrotto, R. N., H. J. Niebauer, J. J. Goering, and R. L. Iverson (1986). Relationships among vertical mixing, nitrate uptake, and phytoplankton growth during the spring bloom in the southeast Bering Sea middle shelf. Continental Shelf Research **5**: 161-198.

Slawyk, G., Y. Collos, and J. C. Auclair (1977). The use of the ^{13}C and ^{15}N isotopes for the simultaneous measurement of carbon and nitrogen turnover rates in marine phytoplankton. Limnology and Oceanography **22**: 925-932.

Shoaf, W. T. and B. W. Lium (1976). Improved extraction of chlorophyll-*a* and -*b* from algae using dimethyl sulfoxide. Limnology and Oceanography **21**: 926-928.

Springer, A. M., C. P. McRoy, and M. V. Flint (1996). The Bering Sea Green Belt: shelf-edge processes and ecosystem production. Fisheries Oceanography **5**: 205-223.

Sunda, W. G. (2001). Bioavailability and bioaccumulation of iron in the Sea. The biogeochemistry of iron in seawater. Vol. 7, D. R. Turner and K. A. Hunter (eds.). New York, John Wiley & Sons, Ltd. 41-84.

Takeda, S. (1998). Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. Nature **393**: 774-777.

Uz, B. M, J. A. Yoder, and V. Osychny (2001). Pumping of nutrients to ocean surface waters by the action of propagating planetary waves. Nature 409:597-600

Wheeler, P. A. and S. A. Kokkinakis (1990). Ammonium recycling limits nitrate use in the oceanic subarctic Pacific. Limnology and Oceanography. **35**: 1267-1278.

Whitledge, T. E., W. S. Reeburgh, and J. J. Walsh (1986). Seasonal inorganic nitrogen distributions and dynamics in the southeastern Bering Sea. Continental Shelf Research **5**: 109-132.

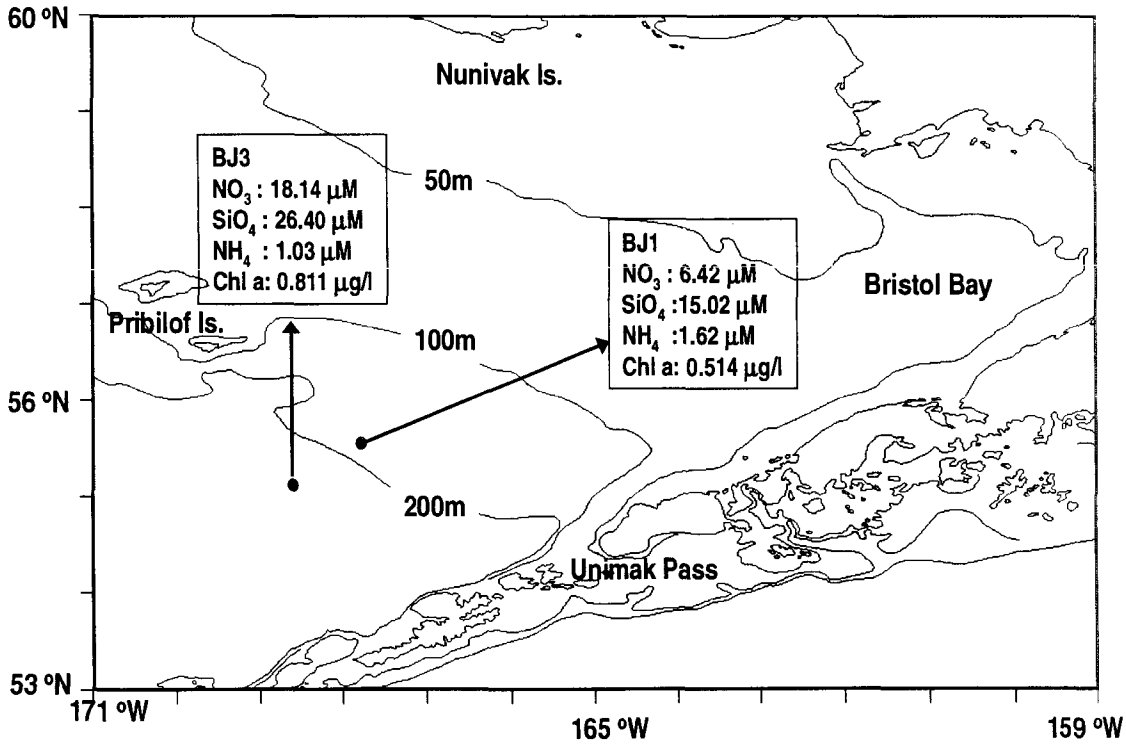

Fig.4.1. Sampling locations for the experiments. Surface shelf water was collected inside the shelf break (BJ1), and open ocean water was collected outside of the shelf break (BJ3).

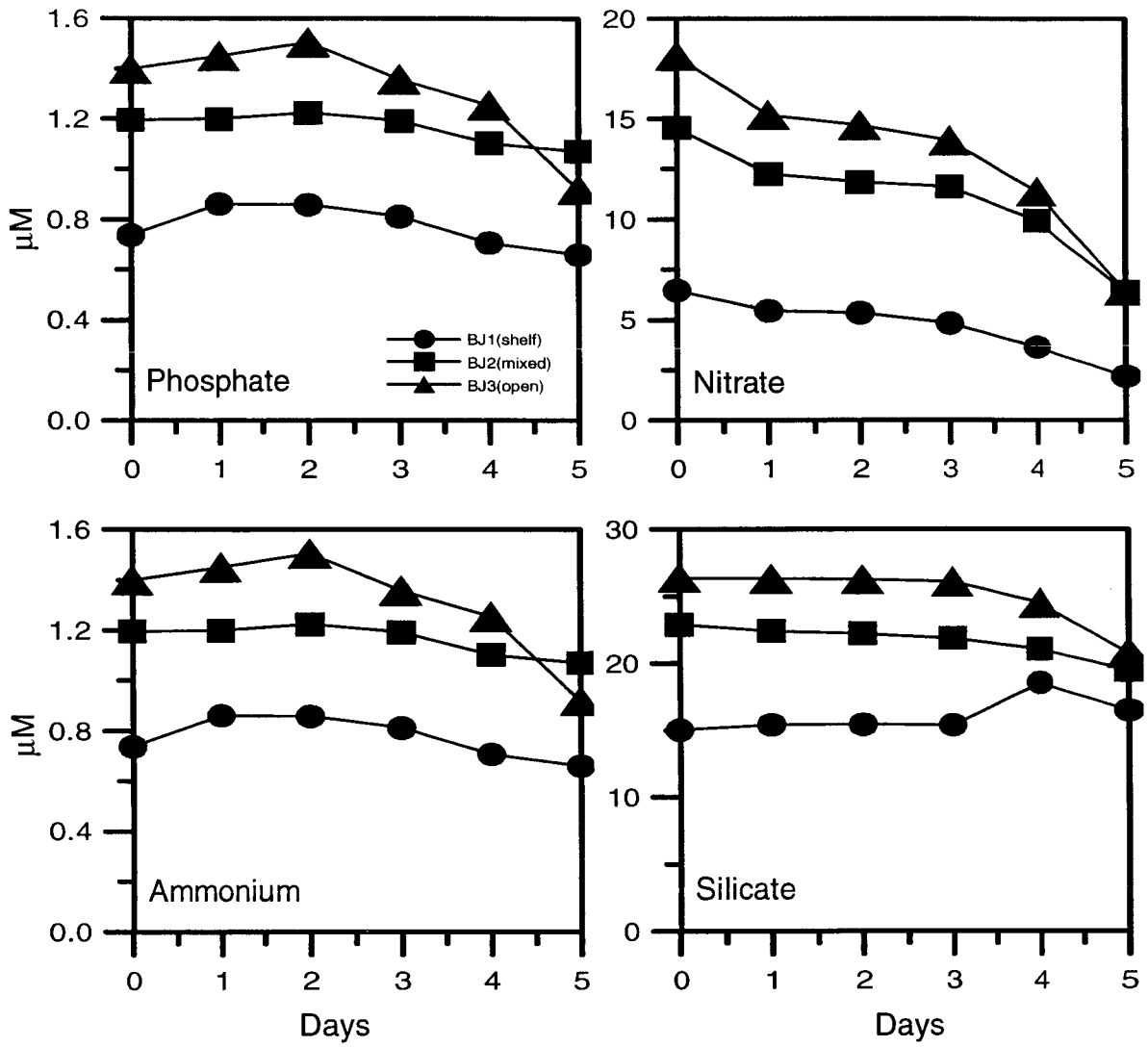

Fig.4.2. Changes of nutrient concentrations during the incubation experiments.

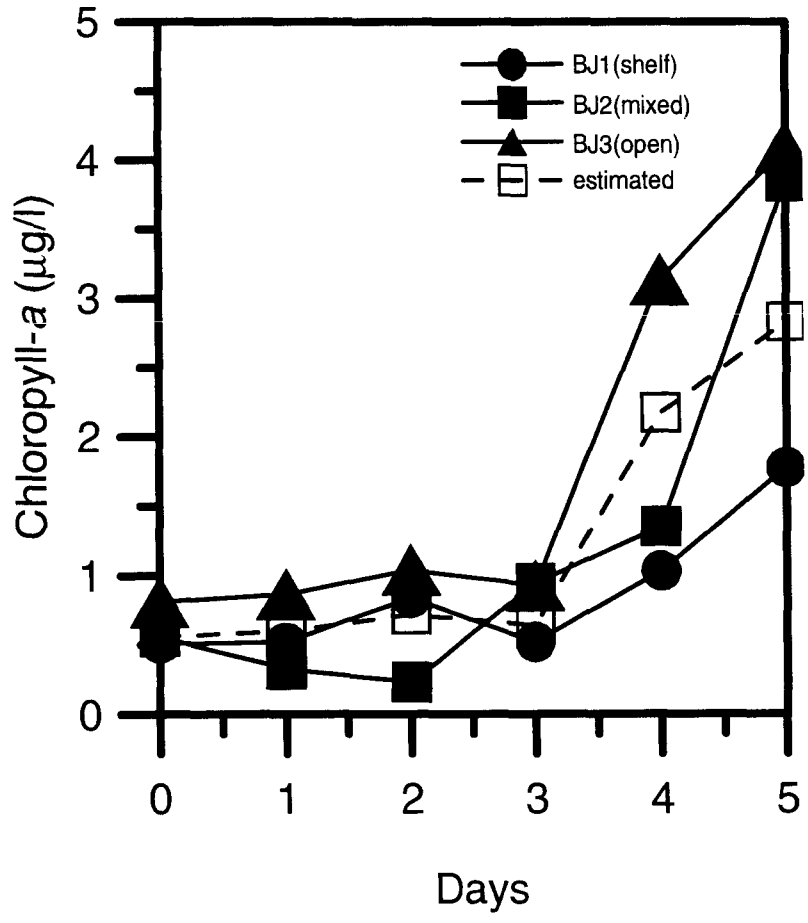

Fig.4.3. Changes of chlorophyll-*a* concentrations over time in the incubation experiments.

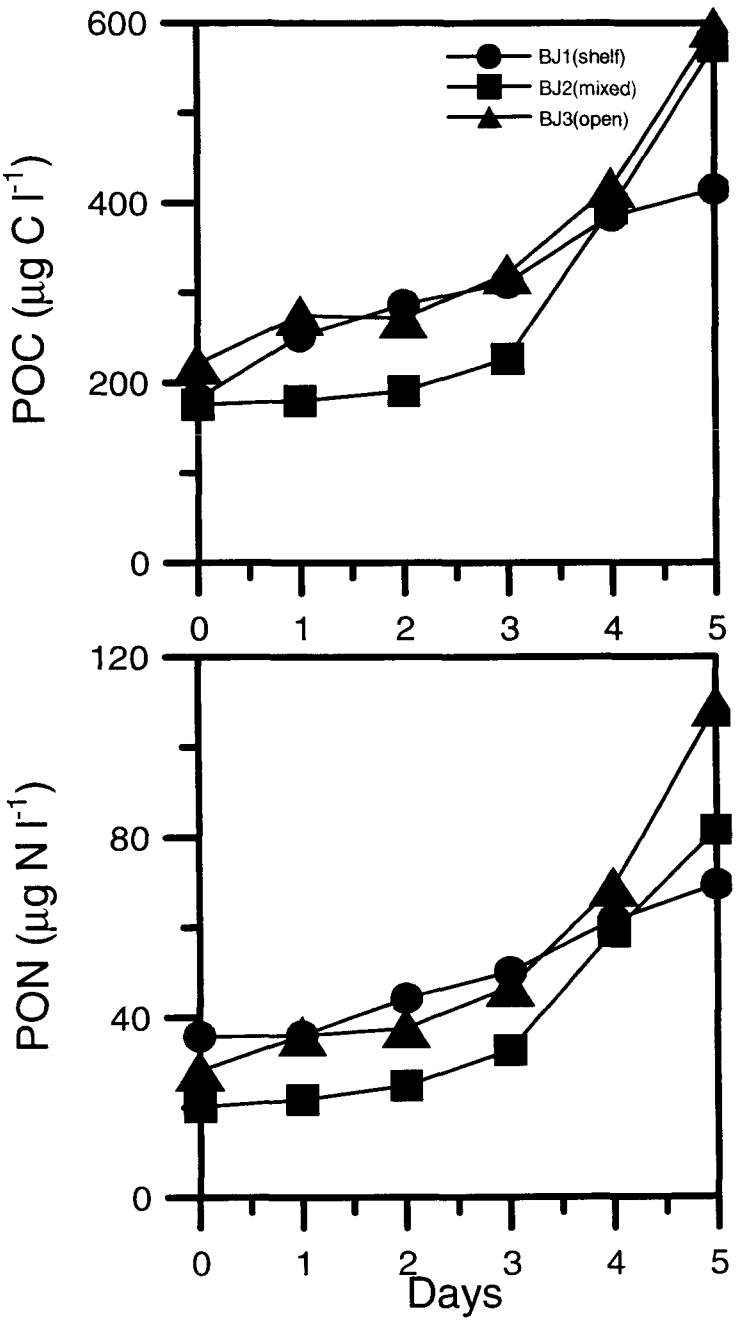

Fig.4.4. Changes of POC and PON concentrations over time in the incubation experiments.

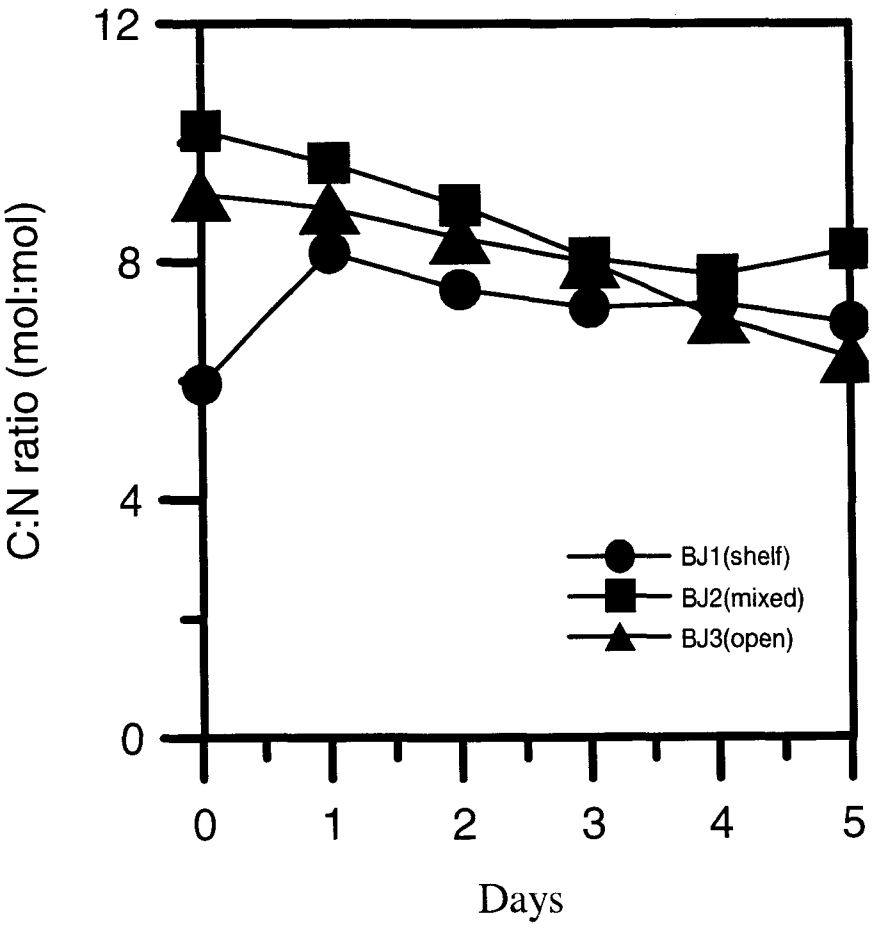

Fig.4.5. Changes of the C:N molar ratio over time in the incubation experiments.

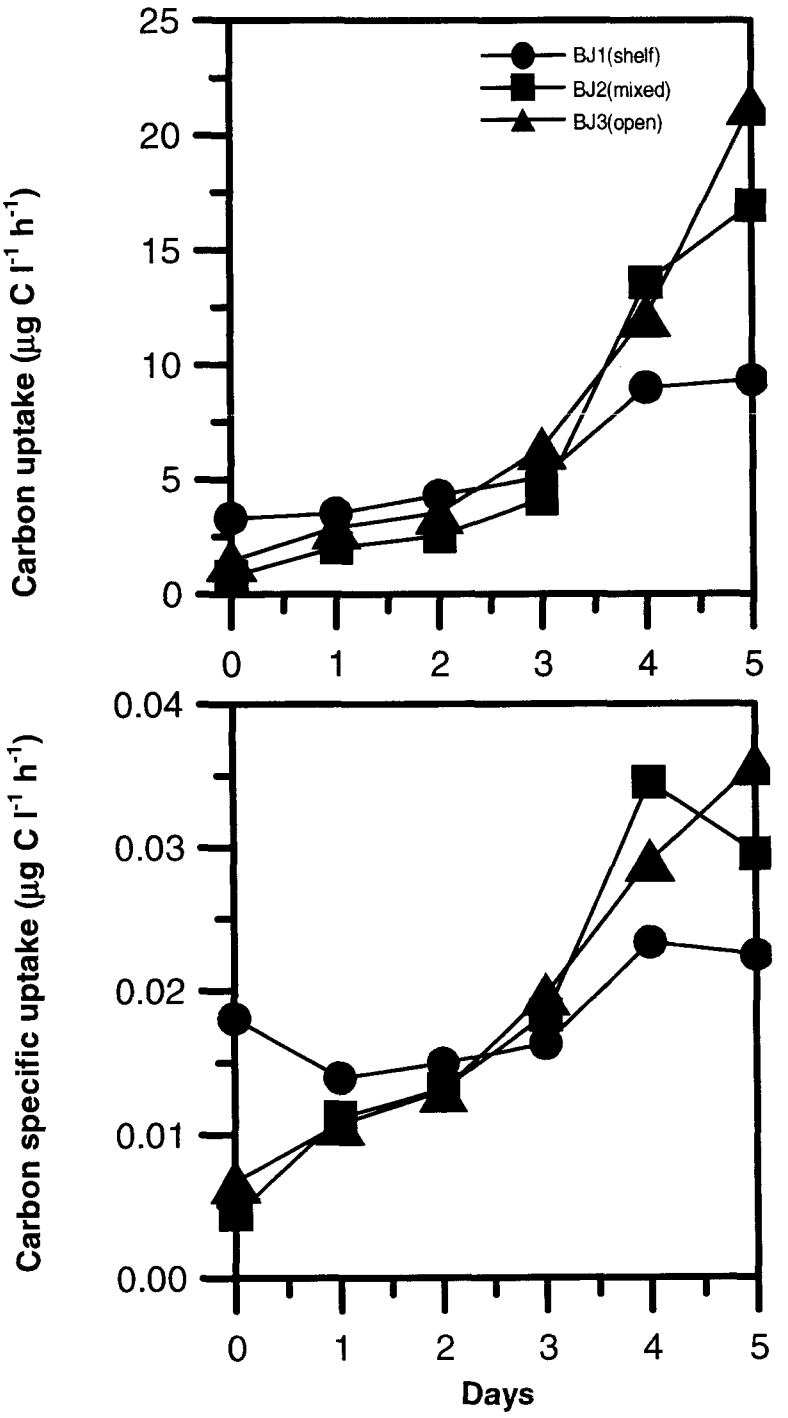

Fig.4.6. Changes of absolute (upper) and specific (lower) carbon uptake rates over time in the incubation experiments.

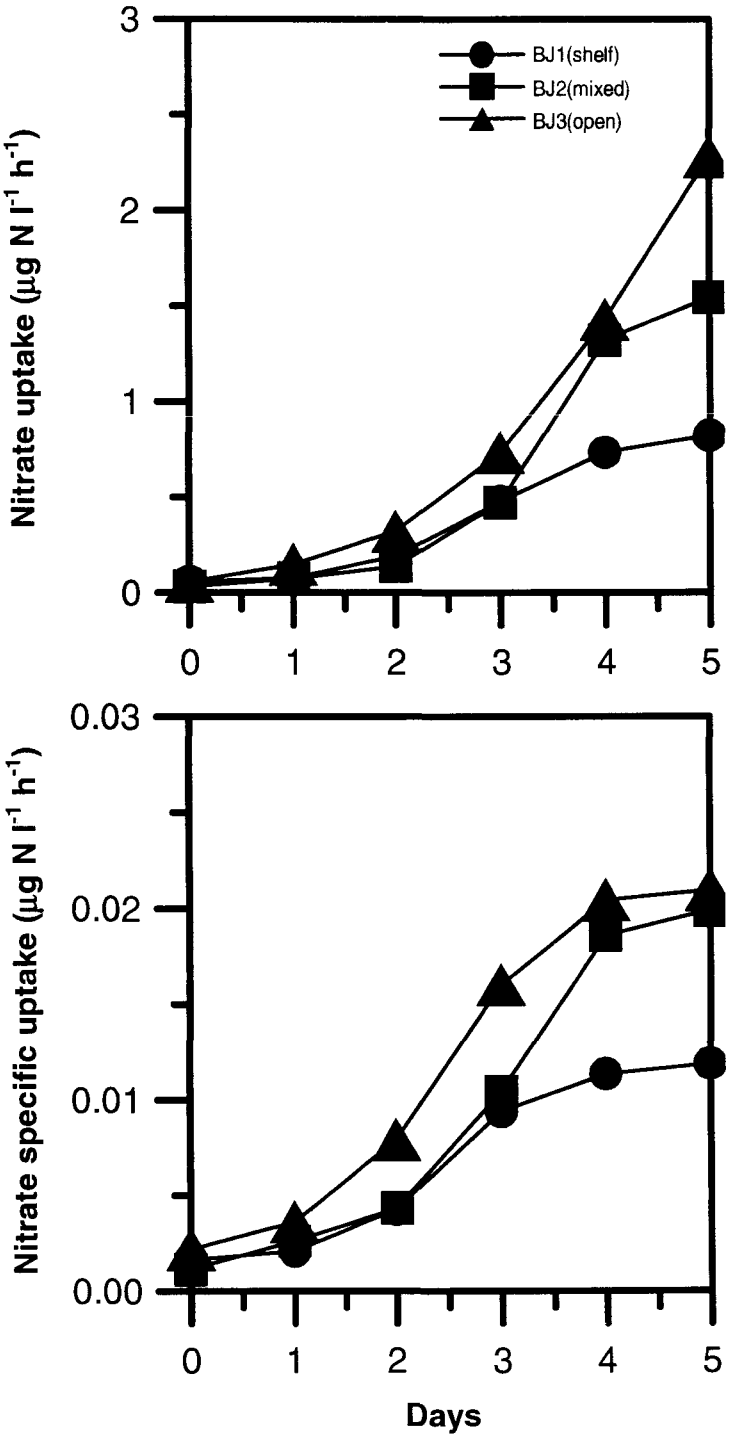

Fig.4.7. Changes of absolute (upper) and specific (lower) nitrate uptake rates over time in the incubation experiments.

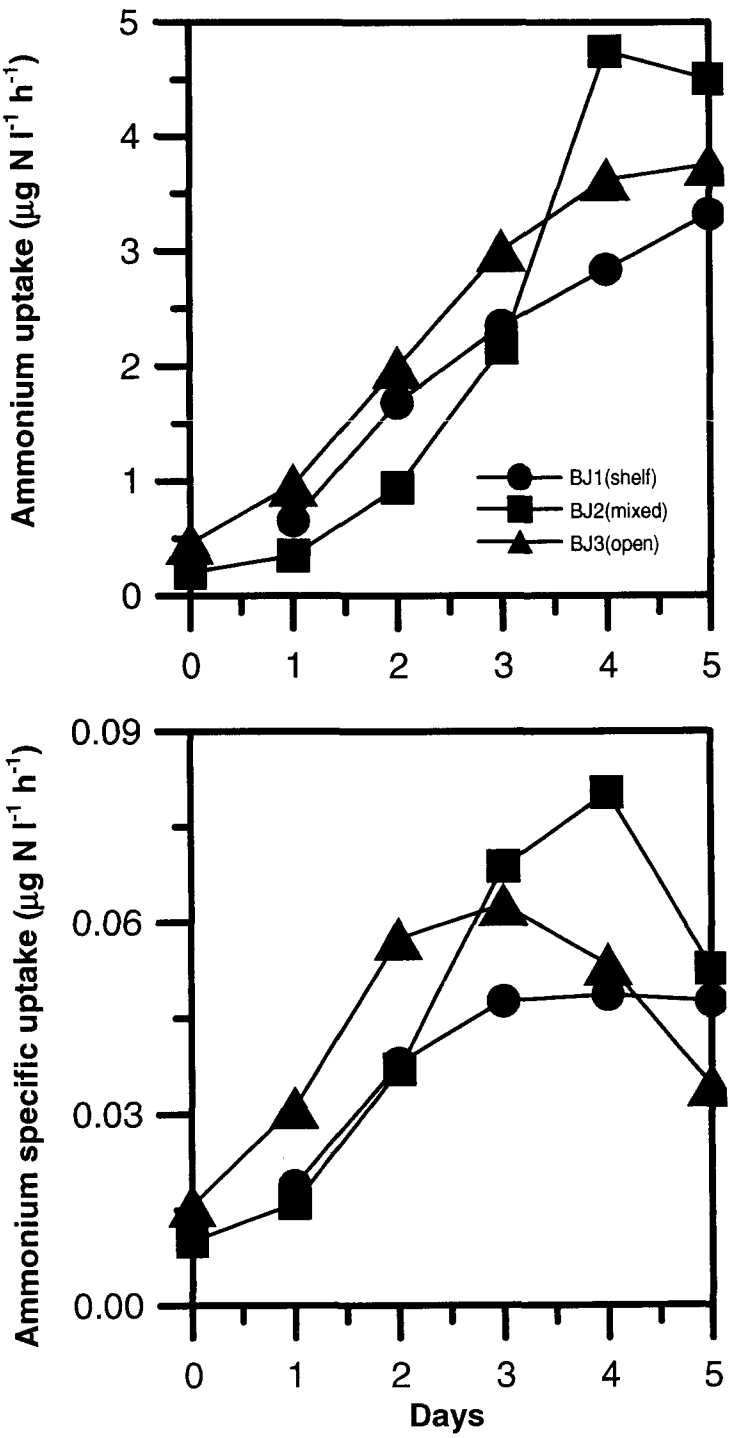

Fig.4.8. Changes of absolute (upper) and specific (lower) ammonium uptake rates over time in the incubation experiments.

Table 4.1. Chlorophyll-*a* specific growth rate, nitrate consumption, POC increase, PON increase, Si:Chl-a, Si:NO_3^-, and NO_3:PO_4^{3-} for the shelf water, the mixed water, and the open ocean water. Si:Chl-*a* is the ratio of Si used and Chl-*a* produced. Si: NO_3^-=Si used: NO_3^- used. NO_3^-:PO_4= NO_3^-used: PO_4^{3-} used. Nitrate consumption rates were calculated by subtracting the final value from the initial value. The increases of POC and PON were calculated by subtracting the initial values from the final values.

Treatments	Chl growth rate(d^{-1})	ΔNO_3^- (µmol/l)	Δ POC (µmol/l)	Δ PON (µmol/l)	Si:Chl*a* (mol:g)	Si:NO_3^- ($molmol^{-1}$)	NO_3^-:PO_4^{3-} ($molmol^{-1}$)
Shelf water	0.252	4.27	19.40	2.40	-	-	55.08
Mixed water	0.656	8.13	33.12	4.39	1.04	0.42	64.53
Open water	0.656	11.69	31.24	5.77	1.71	0.48	24.28

Chapter 5. Iron Addition Experiments Conducted in the Southeastern Bering Sea Middle Shelf and Open Ocean Regions During the Spring of 2001

Abstract

Two shipboard Fe-enrichment experiments were conducted in May 2001 (middle shelf experiments) and June 2001 (open ocean experiment) in the southeastern Bering Sea. Measures of phytoplankton biomass such as chlorophyll-*a*, particulate organic carbon (POC), and particulate organic nitrogen (PON) did not respond to the addition of Fe at the shelf station. Instantaneous uptake rates of carbon and nitrogen showed no apparent differences between treatments in the shelf region experiments. In the open ocean experiment, chlorophyll-*a* concentration enhancement was observed, although other biomass indices such as POC and PON were unchanged. Instantaneous uptake rates of carbon and nitrate showed Fe-meditated enhancement in the open ocean experiment but showed no enhancement in the middle shelf experiment. However, there was no Fe-meditated change in the total amount of nitrate consumption at either the middle shelf or the open ocean stations. Carbon and nitrogen normalized uptake rates showed a similar enhancement, suggesting that the increases of carbon and nitrate uptake rates were not simply due to the increase of biomass, but due to a change in phytoplankton physiology. Our results suggest that the growth of phytoplankton may not be limited by the availability of iron in the middle shelf region, but may be slightly suppressed by the lack of iron in the open ocean.

Keywords: southeastern Bering Sea, shelf break region, iron enrichment, nutrient utilization, carbon and nitrogen uptake rate

5.1. Introduction

During the last decade, there have been a number of research projects undertaken to understand the occurrence of high nitrate/low chlorophyll-a (HNLC) conditions in the surface layer of various open ocean regions, such as the eastern equatorial Pacific, the subarctic Pacific, and the Southern Ocean. After vigorous debates, many of the results were combined into the Ecumenical Iron Hypothesis (Morel *et al.* 1991; Price *et al.* 1994; Cullen 1995; Landry *et al.* 1997). This hypothesis states that, since large phytoplankton have a high iron demand and small phytoplankton have a lower iron demand, low iron concentrations limit the growth of large phytoplankton while providing favorable conditions for the growth of small phytoplankton. Nevertheless, the biomass of small phytoplankton remains low, due to the balance between high growth rates and efficient grazing by protistan grazers (Miller *et al.* 1991; Landry *et al.* 1997).

The importance of iron in controlling the growth of phytoplankton is not confined to remote open ocean regions. A recent series of Fe enrichment experiments in coastal upwelling regions showed that, even in coastal regions, different levels of iron limitation exist, from Fe-replete conditions to severely Fe-limited conditions. Fe enrichment treatments in these coastal regions resulted in various responses in biomass, phytoplankton species, and nutrient biogeochemistry due to different ambient Fe concentrations (Hutchins and Bruland 1998; Hutchins *et al.* 1998; Hutchins *et al.* 2002). These findings are very important in understanding phytoplankton community structure, food web dynamics, and carbon cycling in highly productive coastal upwelling regions.

The Bering Sea shelf is famous for its high productivity in the upper trophic levels, especially commercial fish stocks and marine mammals, but there is a lack of understanding of the dynamics of lower trophic levels processes. The Bering Sea consists of a deep Bering Sea basin and a very wide continental shelf. These two regions are divided by a shelf break region, which is known for higher annual primary and secondary production than the two adjacent regions (Springer *et al.* 1996; Flint *et al.* 2002). Further, the biological processes in the shelf break region are affected by the biological and chemical conditions of the two adjacent regions. Several physical processes, such as intensive tidal mixing, transverse circulation, and eddies in the Bering Slope Current, contribute to the occurrence of high production over the shelf break region by introducing high concentrations of nutrients from deep water into the euphotic zone. However, the detailed mechanisms are unknown (Springer *et al.* 1996). Recently, it has been suggested that the mixing of high nutrient/low Fe basin water with low nutrient/high Fe shelf water may be a plausible mechanism for high primary production over the shelf break region (McRoy *et al.* 2001).

Due to the lack of iron concentration data, it is very uncertain whether the availability of Fe affects the growth of phytoplankton in the Bering Sea. However, several pieces of evidence suggest that low Fe availability may result in HNLC conditions in the deep Basin during summer, while Fe-replete conditions in the shelf region enable a spring phytoplankton bloom that completely utilizes nutrients within the surface layer (Whitledge *et al.* 1986; Banse and English 1999; Fujishima *et al.* 2001). A Fe enrichment study conducted in the coastal upwelling area off California showed that

the growth of phytoplankton is limited when the Fe concentrations are less than 1 nM (Hutchins *et al.* 1998). Low Fe concentrations (< 0.8 nM) occurred in the surface layer over the deep Bering Sea basin during summer (Koike *et al.* 2001). Thus, the growth of phytoplankton may be limited by the low Fe concentration. A low silicate: nitrate ratio occurred in the surface layer of the deep Bering basin during the summer 1997 (Koike *et al.* 2001), which may also indicate the growth of diatoms under Fe limited conditions. Several studies have shown high silicate: nitrate consumption by diatoms under Fe limited conditions (Hutchins and Bruland 1998; Hutchins *et al.* 1998; Takeda 1998). Other explanations cannot be excluded, however, such as the utilization of regenerated nitrogen in the deep Bering Sea basin (Koike *et al.* 2001). As shown in chapter 4, the growth of phytoplankton over the outer shelf and shelf break region may not be limited by the availability of Fe.

In this study, two Fe addition experiments were conducted using water samples collected over the middle shelf and in the open ocean to evaluate the status of Fe limitation in the Bering Sea. In the middle shelf experiment, the effect of different nitrogen treatments on the growth of phytoplankton was also tested. Three different nitrogen treatments (control and either nitrate or ammonium addition) were used. For each nitrogen treatment, two different Fe enrichments (no Fe addition and Fe addition) were used. In the open ocean experiment, the main focus of experiment was the effects of Fe. So three control treatments, three Fe enrichment treatments, and two +Fe+NO_3^- +Si treatments were conducted. Daily for each experiments we measured nutrient

concentrations, chlorophyll-*a*, particulate organic carbon (POC), particulate organic nitrogen (PON), and ^{13}C-, $^{15}NO_3^-$ -, and $^{15}NH_4^+$ - uptake rates.

5.2. Materials and Methods

5.2.1. Water collection and shipboard incubations

For the shipboard Fe addition experiments using middle shelf and open ocean water, surface water was collected on 29 May 2001 from the middle shelf region (M2 site, 56.87 °N 164.05 °W, 70m) and on 3 June 2001 from the open ocean region (56.02 °N 169.75 °W, 3090m) using Niskin bottles mounted on a rosette sampler. Water was transferred from the Niskin bottles through a 333 μm screen to a 10L polycarbonate container. In the middle shelf experiment, water samples were treated with nitrogen and Fe (control, +Fe, $+NO_3^-$, + NO_3^-+Fe, $+NH_4^+$, and + NH_4^++Fe). For the nitrogen treatments, stock solutions of nitrate and ammonium (10ml of 20 μmol NO_3^-/mL or 10mL of 5 μmol NH_4^+/ml) were added into 10L polycarbonate jugs to make 25 μM of nitrate and 10 μM of ammonium. For the Fe enrichment treatment, stock $FeCl_3$ solution (1mL of 10 nmole $FeCl_3$ /mL) was added to make a final concentration around 0.8 nM. However, final Fe concentration was not known, as ambient Fe levels were not measured. In the open ocean experiment, eight treatments (triplicates of the control and Fe enrichment treatments and a duplicate of $+NO_3^-$+SiO_2+Fe treatments) were used. The same amount of the nitrate and Fe stock solutions was the same as in the middle shelf experiment. For the silicate addition, stock silicate solution (5mL of 20 μmole SiO_2/mL) was added to yield a silicate concentration around 7 μM.

Incubation was conducted for 4-5 days in a deck incubator with running surface seawater under 100% ambient light levels. During incubation, subsamples were taken from the 10L incubation jugs daily and nutrients, chlorophyll-*a*, POC, and PON concentrations were measured. Carbon and nitrogen uptake rates were also measured using $H^{13}CO_3^-$, $^{15}NO_3^-$ -, and $^{15}NH_4^+$ stable isotope techniques.

5.2.2. Nutrient analysis

Nutrient concentrations in all water samples were measured on board according to the methods of Whitledge *et al.* (1981) need to add this reference, using automated continuous flow analyzers.

5.2.3. Chlorophyll-*a* analysis

Subsamples (200-300mL) for chlorophyll analysis were taken daily and filtered through GF/F filters. The filters were kept in a freezer until extraction of pigments using an acetone/DMSO procedure (Shoaf and Lium 1976). Concentrations of chlorophyll-*a* were determined fluorometrically using a Turner Designs Model 10-005RU Fluorometer (Parsons *et al.* 1984).

5.2.4. Carbon and nitrogen uptake rates

Subsamples for carbon and nitrogen uptake were transferred to polycarbonate bottles (300mL), which were inoculated according to a double labeling technique (Slawyk *et al.* 1977). We kept the incubation bottles in an on-deck incubator with circulating surface seawater. After incubation for 4 hr, the samples were filtered through precombusted (at 450° C for 4hr) GF/F filters. The filters were frozen until analysis in the Fairbanks laboratory.

5.2.5. POC, PON, and isotope analysis

In the laboratory, the filters were fumed with concentrated hydrochloric acid to remove inorganic carbon, and were subsequently dried at 60° C for 24 hr. Isotope ratios and POC and PON concentrations of the samples were analyzed using a Finigan Delta+XL IRMS. The equation of Dugdale and Goering (1967) was used to calculate carbon and nitrogen uptake rates. The isotopic dilution effect was not considered in uptake calculation because of the short incubation period (Glibert *et al.* 1982).

5.3. Results

5.3.1. Middle shelf experiment

5.3.1.1. Nutrients and nutrient biogeochemistry

Nutrient consumption rates showed slight differences between various nitrogen treatments, but did not respond to Fe enrichment in the middle shelf experiments (Fig.5.2 and Table 5.1). Ambient nitrate concentrations (4.31-5.74 μM) were generally depleted within 2-3 days in the control and ammonium treatment, regardless of Fe enrichment (Fig.5.2). Nitrate concentrations were not depleted until day 4 in the nitrate addition bottles. The utilization of nitrate in the ammonium addition bottles was slightly delayed compared with that in the non-nitrogen treatments (Fig.5.2). Silicate concentrations were completely depleted within 3 days in all treatments. Silicate consumption rates did not vary due to differing nitrogen treatments or Fe enrichment (Fig.5.2). Ambient ammonium concentrations did not show large differences in the control and nitrate treatment, but as expected were greater for the ammonium addition. In the ammonium addition bottles, ammonium concentrations decreased slowly until day 2 and then decreased rapidly, when nitrate concentrations were depleted. The utilization of

phosphate was not affected by the +Fe treatment in any of the nitrogen treatments, but was faster in nitrogen treatments on day 3 than in the non-nitrogen treatments (Fig.5.2). Phosphate concentrations increased in all treatments on day 4 relative to on day 3, suggesting the occurrence of active remineralization.

Net community nutrient utilization, as indicated by $Si(OH)_4$:NO_3^- (Si:N) and NO_3^-:PO_4^{3-} utilization ratios, showed no response to Fe enrichment, but were changed by different nitrogen treatments (Table 5.1). The Si:N utilization ratios were about 1.39 and 1.49 in the control and the NH_4 treatment, respectively (Table 5.1). $Si(OH)_4$:NO_3^- utilization ratios were 1.42 and 1.51 in the +Fe treatment and the NH_4^++Fe treatment, respectively. The $Si(OH)_4$:NO_3^- utilization ratio was very low (0.42) in the nitrate addition bottles. Similar low $Si(OH)_4$:NO_3^- ratios were observed in the subantarctic Southern Ocean (Hutchins *et al.* 2001) and in experiments conducted off the coast of the South America (Hutchins *et al.* 2002), where nonsiliceous taxa and small pennate diatoms were dominant. The NO_3^-:PO_4^{3-} utilization ratios showed no apparent change due to Fe addition within the same nitrogen treatment, but showed large increases (23.84 and 25.97 in the + NO_3^- and the + NO_3^-+Fe treatments, respectively) due to nitrate addition. The NO_3^-:PO_4^{3-} utilization ratios were slightly higher in the control (8.87) than in the ammonium addition (7.39), but were lower than the Redfield value (16).

5.3.1.2. Chlorophyll-*a*, POC, and PON

In the middle shelf region, chlorophyll-*a* concentrations on day 3 were enhanced by nitrogen treatments. The chlorophyll-*a* concentrations were not enhanced by +Fe treatment in the non-nitrogen treatment but were enhanced by +Fe treatment in the nitrate

and ammonium treatments (Fig.5. 3). In the control bottles, chlorophyll-*a* concentrations slightly increased on day 3 (22-32%) compared to initial values and were not affected by +Fe treatment. In the nitrogen treatments (+NO_3^- or +NH_4^+), chlorophyll-*a* concentrations on day 3 had increased more (1.21 to 1.27-fold) than in the control. In each nitrogen treatment, chlorophyll-*a* concentrations on day 3 were enhanced by +Fe treatment (Fig.5.3). Chlorophyll-*a* specific growth rates showed the most response to the nitrogen addition and Fe enrichment in the middle shelf experiment (Table 5.1). Chlorophyll-*a* specific growth rates were higher in the nitrogen treatment (1.86 to 2.13-fold) than in the control treatment. The +Fe treatment enhanced the chlorophyll-*a* specific growth rates (about 1.42 to 1.67-fold) compared with nitrate or ammonium treatments alone. However, +Fe only treatments did not increase the chlorophyll-*a* specific growth rates when compared with the control treatment (Table 5.1).

The responses of POC concentrations to nitrogen and Fe additions were slightly different between day 3 and day 4 in the middle shelf experiment (Fig.5.3; Table 5.1). POC concentrations reached maximum values on day 3 and then slightly decreased on day 4 in non-nitrogen treatments, but continued to increase on day 4 in the nitrogen treatments, regardless of Fe addition (Fig.5.3). In the non-nitrogen treatments, POC production was not affected by +Fe treatment and showed no difference between day 3 and day 4 (Fig.5.3; Table 5.1). In the nitrogen treatments, POC production was not affected by the addition of nitrogen until day 3, but was enhanced by the addition of nitrate (1.94-fold) and ammonium (2.40-fold) on day 4 (Table 5.1). The addition of Fe enhanced POC production on day 3 in the nitrate (1.21-fold) and the ammonium (1.33-

fold) treatments, but the enhancement of POC production by +Fe treatment disappeared on day 4 (Fig.5.3).

The responses of PON concentration to nitrogen and +Fe treatment were different from those of POC in the middle shelf experiment (Fig.5.3; Table 5.1). The +Fe treatment did not enhance PON production in the non-nitrogen treatment. The addition of nitrogen enhanced PON production on both day 3 and day 4. The +Fe treatment enhanced PON production in the nitrate (1.16-fold) and in the ammonium treatments (1.23-fold) on day 3. On day 4, the enhancement of PON production by +Fe occurred only in the nitrate treatment (1.24-fold). The initial C:N molar ratio in the middle shelf water was slightly higher (7.4) than the Redfield value (6.6). C:N molar ratios increased in the non-nitrogen treatment, but generally decreased in the nitrogen treatment (Fig.5.3).

5.3.1.3. Carbon and nitrogen uptake rates

In the middle shelf experiment, there was no marked difference in absolute and specific ^{13}C uptake rates due to nitrogen and Fe treatment until day 3. On day 4, absolute and specific ^{13}C uptake rates showed a slight difference due to the nitrogen treatments (Fig.5.4). In the non-nitrogen treatments, absolute ^{13}C uptake rates reached a maximum value on day 3 and decreased rapidly on day 4. In the nitrogen treatments, absolute ^{13}C uptake rates were similar to those for the non-nitrogen treatments until day 3, but increased to higher values compared with the non-nitrogen treatment on day 4 (Fig.5.4). The response of specific ^{13}C uptake rates to nitrogen and +Fe treatments was similar to that of absolute ^{13}C uptake rates, but the maximum specific ^{13}C uptake rate occurred on day 2 in all treatments and generally decreased with time (Fig.5.4).

Absolute and specific $^{15}NO_3^-$ uptake rates were not affected by +Fe treatment within the same nitrogen treatment, but were enhanced or depressed by different nitrogen treatments (Fig.5.4). In the non-nitrogen treatments, absolute $^{15}NO_3^-$ uptake rates generally decreased as nitrate concentrations were depleted with time, except for the large increase on day 3 (Fig.5.4). The mean absolute $^{15}NO_3^-$ uptake rate increased in the nitrate treatment (1.87-fold) compared to non-nitrogen treatments. The mean absolute $^{15}NO_3^-$ uptake rate decreased about 28% in the ammonium treatments compared to non-nitrogen treatments. This supports the idea that ammonium is inhibiting nitrate uptake (Wheeler and Kokkinakis 1990). In the nitrogen treatments, maximum specific $^{15}NO_3^-$ uptake rates of each treatment occurred on day 0, and generally decreased as nitrate concentration decreased. However, the occurrence of maximum uptake rates on day 3 in the non-nitrogen treatments was unusual. The responses of specific $^{15}NO_3^-$ uptake rates to the different nitrogen treatments and +Fe treatment were the same as the absolute $^{15}NO_3^-$ uptake rates (Fig.5. 4)

Absolute and specific $^{15}NH_4^+$ uptake rates showed no marked changes due to nitrogen and +Fe treatments (Fig.5.4). Absolute $^{15}NH_4^+$ uptake rates generally increased with time in all treatments, but specific $^{15}NH_4^+$ uptake rates did not show an increasing trend (Fig.5.4). Nitrate treatment decreased mean $^{15}NH_4^+$ uptake rates about 35% compared to non-nitrogen treatments. Specific $^{15}NH_4^+$ uptake rates showed a slight depression in the nitrate treatment compared to the non-nitrogen treatment (Fig.5.4).

5.3.2. Open ocean experiment

5.3.2.1. Nutrient and nutrient biogeochemistry

Nitrate concentrations in all treatments were depleted within 3-4 days. The nitrate concentration on day 2 was 1.9-fold higher in the control (3.57 ± 0.46 μM) than in the Fe enrichment (1.86 ± 0.16 μM), although total nitrate consumption was similar in both the control and the +Fe treatment (Fig.5.5; Table 5.2). The addition of nitrate resulted in a higher nitrate consumption rate compared with the control and the +Fe treatments, due to the increase of nitrate availability. Silicate concentrations were very low (< 1 μM) in the water column from which the water for experiments was collected. Silicate concentrations were maintained at low levels in the control and the +Fe treatment throughout the open ocean experiment. The change of silicate concentration was too small to compare the consumption rates between the control and Fe enrichment. In the +Fe+NO_3^-+Si treatment, the silicate consumption rate was very slow on day 1 (0.69 ± 0.46 μM d^{-1}), but increased on day 2 (8.48 ± 0.06 μM d^{-1}) (Fig. 5.5). Ammonium concentrations were low (< 1 μM) in the early part of the experiment (until day 2), but were high (>4 μM) in the later part of the experiment. +Fe treatment resulted in faster phosphate utilization compared to the control. Phosphate concentrations generally decreased with time, but were not depleted on day 4. As observed with ammonium concentrations, active remineralization might be responsible for maintaining phosphate concentrations on day 4 in the open ocean experiment.

The effect of +Fe treatment on net community $Si(OH)_4$:NO_3^- utilization ratios could not be assessed due to the low initial silicate concentration in the control and +Fe

treatment. However, the net community $Si(OH)_4$:NO_3^- utilization ratio in the +Fe+NO_3+Si treatment (0.46) was very close to that of the nitrate addition bottles from the middle shelf experiment (0.42). Unlike the middle shelf experiments, NO_3^-:PO_4^{3-} utilization ratios were very close to the Redfield value in the control and the +Fe treatment (Table 5.2). This suggests that nitrate fulfilled the nitrogen requirement of phytoplankton in the open ocean experiment. The NO_3^-:PO_4^{3-} utilization ratio in the nitrate addition experiment was 2.3-fold higher than the Redfield value, due to increased nitrate availability.

5.3.2.2. Chlorophyll-*a*, POC, and PON

In the open ocean experiment, chlorophyll-*a* concentrations were enhanced by the +Fe treatment (Fig.5.6; Table 5.2). Chlorophyll-*a* concentrations were nearly unchanged in the control treatment, but increased to about 1.6-fold and 3-fold in the +Fe treatment and the +Fe+NO_3+Si treatment, respectively (Fig.5.6; Table 5.2). Chlorophyll-*a* concentrations in the +Fe treatment reached a maximum value (3.87 ± 0.34 μg chl l^{-1}) on day 2 and remained at a similar value on day 4 (3.67 ± 0.53 μg chl l^{-1}). However, the chlorophyll-*a* concentration increased continuously and reached a maximum value on day 4 in the +Fe+NO_3^-+Si treatment. Similar to the middle shelf experiment, chlorophyll-*a* specific growth rates increased in the +Fe treatment (3-fold) and in the +Fe+NO_3^-+Si treatment (7.7-fold) compared to the control treatment (Table 5.2).

Unlike the effect of the +Fe treatment on chlorophyll-*a* concentrations, POC and PON concentrations were not significantly affected by the +Fe treatment in the open ocean experiment (Fig.5.6; Table 5.2). POC and PON concentrations in the +Fe

treatment were not different from the control treatment, but in the +Fe+NO_3+Si treatment POC and PON concentrations were higher than in the control and the +Fe treatments (Fig.5.6). POC and PON concentrations continuously increased with time in all treatments, and the increases of POC and PON were more conspicuous in the +Fe+NO_3+Si treatment (Fig.5.6).

The C:N molar ratio on day 0 (7.24± 0.17) was slightly higher than the Redfield value (6.6). The C:N molar ratios showed similar values and generally decreased in all treatments until day 3. After nitrate depletion on day 3, the C:N molar ratios increased on day 4 (Fig.5. 6).

5.3.2.3. Carbon and nitrogen uptake rates

In the open ocean experiment, absolute and specific ^{13}C uptake rates were enhanced by the +Fe and the +Fe+NO_3^-+Si treatments compared to the control treatment (Fig.5.7). In the control treatment, absolute ^{13}C uptake rates reached a maximum value on day 2 and remained at high levels until day 4. The maximum specific ^{13}C uptake rate occurred on day 2 and decreased as nutrients were depleted on day 3 (Fig.5.7). In the +Fe treatment, the absolute ^{13}C uptake rates reached a maximum value on day 2 and decreased rapidly. The +Fe treatment enhanced the absolute ^{13}C uptake rates on day 1 (1.43-fold) and on day 2 (1.89-fold) compared to the control treatment. The specific ^{13}C uptake rates in the +Fe treatment exhibited the same trend as was observed in the control treatment, but significantly increased on day 1 and on day 2 compared to the control treatment. In the +Fe+NO_3^-+Si treatment, the absolute ^{13}C uptake rates showed a similar trend as in the +Fe treatment except for the one-day delay of the maximum value

compared to the +Fe treatment. The mean absolute ^{13}C uptake rate was 1.31 to 1.6-fold higher in the +Fe+NO_3^-+Si treatment than in the control and in the +Fe treatment (Fig.5.7).

Absolute and specific $^{15}NO_3^-$ uptake rates were affected by the +Fe and nutrient (nitrate and silicate) treatments in the open ocean experiment (Fig.5.7). In the control treatment, absolute $^{15}NO_3^-$ uptake rates gradually increased and a maximum value occurred on day 2. A rapid decrease of the absolute $^{15}NO_3^-$ uptake rate occurred on day 3 as nitrate was depleted (Fig.5.5; Fig.5.7). In contrast to absolute $^{15}NO_3^-$ uptake rates, the specific $^{15}NO_3^-$ uptake rate reached a maximum value on day 2 and decreased to a minimum value on day 3 in the control treatment. In the +Fe treatment, the initial absolute $^{15}NO_3^-$ uptake rate was similar to that of the control treatment, and the average absolute $^{15}NO_3^-$ uptake rate increased about 1.76-fold in the +Fe treatment (0.97 ± 0.41 $\mu g\ N\ l^{-1}\ h^{-1}$) compared with the control treatment (0.55 ± 0.29 $\mu g\ N\ l^{-1}\ h^{-1}$). The specific $^{15}NO_3^-$ uptake rate showed a maximum value on day 2. The maximum value in the +Fe treatment was about 1.39-fold higher than in the control treatment (Fig.5.7). In the +Fe+NO_3^-+Si treatment, absolute $^{15}NO_3^-$ uptake rates showed almost the same trend as in the +Fe treatment. An average absolute $^{15}NO_3^-$ uptake rate in the +Fe+NO_3^-+Si treatment was about 2.05-fold higher than that in the control treatment, and was about 1.17-folder higher than that in the +Fe treatment. The specific $^{15}NO_3^-$ uptake rate in the +Fe+ NO_3^-+Si treatment was almost identical to that in the +Fe treatment, but specific $^{15}NO_3^-$ uptake rates were slightly higher on day 1 and on day 2 than in the +Fe treatment.

Absolute and specific $^{15}NH_4^+$ uptake rates in the open ocean experiment showed exactly the same response to the +Fe and the +Fe+ NO_3^-+Si treatments (Fig.5.7). Absolute and specific $^{15}NH_4^+$ uptake rates increased in response to the +Fe treatment and decreased in the +Fe+ NO_3^-+Si treatment compared to the control (Fig.5.7). Large decreases of absolute and specific $^{15}NH_4^+$ uptake rates were observed in the +Fe+ NO_3^- +Si treatment (Fig.5.7).

5.4. Discussion

Results from the Fe and nitrogen addition experiments in the middle shelf region suggest that phytoplankton are growing in Fe-replete conditions, as was described for the California coastal upwelling regions (Hutchins *et al.* 1998). Our results also demonstrate that the growth of phytoplankton was not affected by the +Fe treatment in water samples from the middle shelf, and that the supply of Fe was balanced with that of nitrate in the middle shelf region. Nutrient consumption, chlorophyll-*a* concentrations, and carbon and nitrogen uptake rates were not affected by the Fe addition treatments within the same nitrogen treatments. However, +Fe treatment resulted in slightly higher PON production in the nitrate treatment on day 4. A large increase of the chlorophyll-a concentration and PON production by the nitrogen additions suggests that, in the natural environment, the growth of phytoplankton was not suppressed by the availability of Fe. Si:NO_3^- consumption ratios showed no response to +Fe treatment in the middle shelf region. Our results also suggest that phytoplankton were growing in suboptimal conditions due to meager concentrations of nitrogen. Additional nitrate supply, without more Fe, could not increase productivity because of the lack of Fe in this region.

Our results in the open ocean experiment show that the growth of phytoplankton was not limited by the availability of Fe in ambient water, but was very similar to the classification for a Fe-stressed condition (Type 2) from the California coastal upwelling region (Hutchins *et al.* 1998). Similar to the middle shelf experiment, the total nitrate consumption was not influenced by the +Fe treatment, due to the complete depletion of nitrate by day 3 in the open ocean experiment. However, instantaneous nitrate uptake rates on day 2, measured by the isotope method, were slightly larger in the +Fe treatment than in the control treatment (Fig.5.4). POC and PON production showed no significant differences due to the +Fe treatment, but chlorophyll-*a* specific growth rates and carbon and nitrogen uptake rates were enhanced by the +Fe treatment (Fig.5.7; Table 5. 2). These results suggest that in the open ocean regions phytoplankton grow in suboptimal conditions due to a slight Fe stress.

5.4.1. Effects of +Fe treatment on the nutrient biochemistry

The change of nitrate consumption rates by the +Fe treatment is one of indices of Fe limitation in the water column. Surface nitrate was not utilized completely, due to the lack of the availability of Fe in the traditional HNLC regions such as the northern North Pacific, the equatorial Pacific, and the Southern Ocean (Price *et al.* 1991; Hutchins *et al.* 2001). Many Fe enrichment studies in the HNLC regions showed that nitrate consumption was enhanced in the +Fe treatment compared to the control. In water samples from the California coastal upwelling region, +Fe treatments resulted in various influences because of varying ambient Fe concentrations. Phytoplankton utilized nitrate completely in the control bottles from Fe-replete and Fe-stressed waters, but did not

consume all of the nitrate in those from moderately and severely Fe-limited waters (Hutchins *et al.* 1998).

In the middle shelf and open ocean experiments, nitrate concentrations were depleted by day 3 in both the control and the +Fe treatments (Fig.5.2; Fig.5.5). These results suggest that the utilization of nitrate by phytoplankton was not limited by the availability of Fe. In the middle shelf experiment, nitrate concentrations become depleted even in the nitrate addition treatment, regardless of +Fe treatment. In the open ocean experiment, nitrate concentrations on day 2 were slightly lower in the +Fe treatment than in the control. This suggests that nitrate consumption rates were slightly enhanced on day 2 by the +Fe treatment in the open ocean sample, although total nitrate consumption by day 3 in the +Fe treatment was not different from the control due to complete consumption in both treatments (Fig.5.5).

$Si:NO_3^-$ (Si:N) consumption ratios also provide very useful information about the effect of +Fe treatments on nutrient consumption by phytoplankton. Generally, Si:N consumption ratios of diatoms are close to unity in nutrient replete conditions (Brzezinski 1985), but are 2-3 times higher in Fe limited conditions (Hutchins and Bruland 1998; Takeda 1998). The Si:N consumption ratios suggest that the growth of phytoplankton was not affected by the availability of Fe over the middle shelf. The Si:N consumption ratio was very low (0.42) in the nitrate addition bottles of the middle shelf experiment. In the open ocean experiment, the effects of +Fe treatment on the Si:N uptake rates were very subtle, due to a low ambient silicate concentration (Fig.5.5; Table 5.2). The Si:N consumption ratio in the $+Fe+NO_3^-$+Si treatment was about 0.42, which was similar to

that in nitrate addition bottles over the middle shelf experiment. When nutrients and Fe were replete, low Si:N consumption ratios were observed in both the middle shelf and open ocean experiments, which may be attributed to the dominance of small nanoplanktonic pennate diatoms and/or nondiatom species (Hutchins *et al.* 2001; Hutchins *et al.* 2002).

Initial nitrate concentrations were low (about 5 μM). The NO_3^-:PO_4^{3-} molar ratios were almost half of the Redfield N:P ratios in the control (8.87) and ammonium (7.39) treatments. These ratios indicate that nitrate contributed half of the nitrogen requirement of phytoplankton in the middle shelf region. In nutrient replete conditions including Fe, diatoms utilize nitrate and silicate in a 1:1 ratio (Brzezinski 1985). The Si:N consumption ratios in the control (1.39) and ammonium (1.49) treatments indicate that diatom species, utilizing both silicate and nitrate, may not experience a shortage of nitrate compared to silicate during growth. However, lower Si:N and higher NO_3^-:PO_4^{3-} molar ratios compared to the Redfield ratio occurred in the +NO_3^- treatment, which suggests typically that the phytoplankton community utilized more nitrate than phytoplankton needed for growth (Table 5.1). In spite of high nitrate consumption, POC and PON production were not different from the control. Diatom species could not utilize more nitrate or ammonium nitrogen than was supplied, because there was no additional silicate for continuing growth after day 3 (Fig.5.2).

5.4.2. Effects of +Fe treatment on biomass

Responses of biomass, such as chlorophyll-*a*, POC, and PON concentrations, are widely used to determine the effect of Fe enrichment on the growth of phytoplankton.

The chlorophyll-*a*, POC, and PON concentrations increased in + Fe treatments compared to control treatments in regions where the availability of Fe limits the growth of large phytoplankton (Price *et al.* 1994; Coale *et al.* 1996; Hutchins *et al.* 1998; Hutchins *et al.* 2001).

The responses of biomass in the middle shelf experiment indicate that the growth of phytoplankton was not affected by Fe addition in the non-nitrogen treatment, which suggests that the availability of Fe may not affect the growth of phytoplankton in the middle shelf (Fig.5.3). The response of biomass on the +Fe treatment was very similar to that observed in the Fe-replete area of the California coastal upwelling region, where chlorophyll-*a*, POC, and PON production were not affected by the +Fe treatment (Hutchins *et al.* 1998). In the middle shelf region, higher biomass in the nitrogen treatments (nitrate or ammonium) compared to the control suggests that the availability of nitrogen may limit the later stages of phytoplankton growth (Fig.5.3).

In the open ocean experiment, chlorophyll-*a* concentrations were enhanced by the +Fe treatment without corresponding increases of POC and PON production, which suggests that the addition of Fe may result in an increase of chlorophyll-*a* within cells instead of increasing cell numbers. Hutchins *et al.* (1998) reported the increase of chlorophyll-*a* per cell, without an apparent change of net POC production, by the +Fe treatment in a Fe-stressed area (Type 2 waters in the Four-stage Fe limitation classification) of the California coastal upwelling region.

The production of chlorophyll-*a*, POC, and PON were higher in the +Fe+NO_3^-+Si treatment than in the control or the +Fe treatments (Fig.5.6). This suggests that the

potential growth of phytoplankton in the open ocean region may be limited by the availability of nitrate or silicate. Although it is impossible to estimate the relative importance of nitrate or silicate due to limitation in our experimental design, ambient nutrient concentrations (nitrate ~10 μM, silicate < 1μM) suggest that the growth of phytoplankton may be limited by silicate concentrations that are ultimately caused by Fe limitation (Dugdale and Wilkerson 1998; Hutchins and Bruland 1998; Takeda 1998). The C:N and NO_3^-:PO_4^{3-} molar ratios of the control and the +Fe treatments in the open ocean experiment were similar to the Redfield value. Most of the nitrate consumption appeared as an increase of PON (Table 5. 2). These data also support the possibility of silicate limitation on the growth of phytoplankton in our open ocean experiments. In other studies, Fe limitation resulted in a higher Si:N consumption ratio and accompanied silicate limitation, due to the slow remineralization of silicate compared to nitrogen (Dugdale and Wilkerson 1998; Hutchins and Bruland 1998; Takeda 1998). Several studies of nutrient and surface Fe concentrations indicate the possibility of Fe limitation in the Bering Sea Basin (Fujishima *et al.* 2001; Koike *et al.* 2001).

5.4.3. Effects of +Fe treatment on carbon and nitrogen uptake rates

In the middle shelf experiment, the results of ^{13}C uptake rate measurements suggest that the availability of Fe is not affecting the growth of phytoplankton. However, the additional supply of nitrogen would be very important in the continuous accumulation of biomass (Fig.5.4). ^{13}C uptake rates were not changed by the +Fe only treatment. Nutrient concentrations were depleted by day 3 and ^{13}C uptake rates increased continuously in the nitrogen treatments regardless of the +Fe treatment (Fig.5. 4). If the

Fe supply were limiting in this region, the addition of Fe may have resulted in the increase of ^{13}C uptake rates. In the NE subarctic Pacific, a well known HNLC region, ^{14}C uptake rates and nitrate specific uptake rates showed large differences between the controls and the +Fe treatments (Boyd *et al.* 1996).

$^{15}NO_3^-$ and $^{15}NH_4^+$ uptake rates suggest that the growth of phytoplankton was not controlled by the availability of Fe, but was controlled by the supply of nitrogen in the middle shelf during the late spring period (Fig.5.4). In addition, $^{15}NO_3^-$ uptake rates were not changed by the +Fe treatment in the same nitrogen treatment, but were affected by the different nitrogen treatments regardless of the +Fe treatment. In the HNLC regions, the addition of Fe enhanced nitrate uptake rates compared to the control, while ammonium specific uptake rates were not affected by the +Fe treatment (Boyd *et al.* 1996; Coale *et al.* 1996). Nitrate uptake rates were lower in the ammonium treatment and were higher in the nitrate treatment compared to the control treatment (Fig.5.4). The decrease of nitrate uptake rates in the ammonium treatment may be caused by the inhibition of nitrate uptake rates by ammonium (Wheeler and Kokkinakis 1990). The addition of nitrate also resulted in a slight decrease of ammonium uptake rates, although the decrease was much smaller than the ammonium inhibition of nitrate uptake rate (Fig.5.4).

In the open ocean experiment, the +Fe treatment enhanced $H^{13}CO_3^-$, $^{15}NO_3^-$, and $^{15}NH_4^+$ uptake rates without significant changes of POC and PON concentrations. This indicates that the availability of Fe does not limit growth, but places a slight stress on the physiology of phytoplankton. The response of $H^{13}CO_3^-$ and $^{15}NO_3^-$ uptake to +Fe

treatment was similar to that observed in the Fe limited water experiments in the equatorial Pacific and northern North Pacific. However, $^{15}NH_4^+$ uptake rates in our open ocean experiment were different from other studies conducted in HNLC regions, which showed no apparent response to Fe enrichment in any of the phytoplankton size fractions (Boyd *et al.* 1996). In our open ocean experiment, $^{15}NH_4^+$ uptake rates slightly increased in the +Fe treatment with time. A possible explanation may be that the +Fe treatment resulted in the rapid consumption of nitrate. The resulting PON was then remineralized rapidly and produced more ammonium (Fig.5.5). The increased supply of ammonium could have resulted in the higher ammonium uptake rates in the Fe enrichment bottles compared to the control. The decrease of $^{15}NH_4^+$ uptake rates in the +Fe+NO_3^-+Si treatment may be due to the inhibition of the ammonium uptake rate by the high nitrate concentration in our experiments.

References

Banse, K. and D. C. English (1999). Comparing phytoplankton seasonality in the eastern and western subarctic Pacific and the western Bering Sea. Progress in Oceanography **43**: 235-288.

Boyd, P. W., D. L. Muggli, D. E. Varela, R. H. Goldblatt, R. Chretien, K. J. Orians, and P. J. Harrison (1996). *In vitro* iron enrichment experiments in the NE subarctic Pacific. Marine Ecology Progress Series **136**: 179-193.

Brzezinski, M. A. (1985). The Si:C:N ratio of marine diatoms: Interspecific variability and the effect of some environmental variables. Journal of Phycology **21**: 347-357.

Coale, K. H., K. S. Johnson, S. Fitzwater, R. M. Gordon, S. Tanner, F. P. Chavez, L. Ferioli, C. Sakamoto, P. Rogers, F. J. Millero, P. Steinberg, P. Nightingale, D. Cooper, W. P. Cochlan, M. R. Landry, J. Constantinou, G. Rollwagen, A. Trasvina, and R. Kudela (1996). A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. Nature **383**: 495-501.

Cullen, J. J. (1995). Status of the iron hypothesis after the open-ocean enrichment experiment. Limnology and Oceanography **40**: 1336-1343.

Dugdale, R. C. and J. J. Goering (1967). Uptake of new and regenerated forms of nitrogen in primary productivity. Limnology and Oceanography **12**: 196-206.

Dugdale, R. C. and F. P. Wilkerson (1998). Silicate regulation of new production in the equatorial Pacific upwelling. Nature **391**: 270-273.

Flint, M. V., I. N. Sukhanova, A. I. Kopylov, S. G. Poyarkov, and T. E. Whitledge (2002). Plankton distribution associated with frontal zones in the vicinity of the Pribilof Islands. Deep-Sea Research II **49**: 6069-6093.

Fujishima, Y., K. Ueda, M. Maruo, E. Nagayama, C. Tokutome, H. Hasegawa, M. Matsui, and Y. Sohrin (2001). Distribution of trace bioelements in the subarctic North Pacific Ocean and the Bering Sea (the R/V Hakuho Maru Cruise KH-97-2). Journal of Oceanography **57**: 261-273.

Glibert, P. M., J. J. Lipschultz, J. J. McCarthy, and M. A. Altabet (1982). Isotope dilution models of uptake and remineralization of ammonium by uptake and remineralization of ammonium by marine plankton. Limnology and Oceanography **27**: 639-650.

Hutchins, D. A. and K. W. Bruland (1998). Iron-limited diatom growth and Si:N uptake ratios in a coastal upwelling regime. Nature **393**: 561-564.

Hutchins, D. A., G. R. DiTullio, Y. Zhang, and K. W. Bruland (1998). An iron limitation mosaic in the California upwelling regime. Limnology and Oceanography **43**: 1037-1054.

Hutchins, D. A., C. E. Hare, R. S. Weaver, Y. Zhang, G. F. Firme, G. R. DiTullio, M. B. Alm, B. F. Riseman, J. M. Maucher, M. E. Geesey, C. G. Trick, G. J. Smith, E. L. Rue, J. Conn, and K. W. Bruland (2002). Phytoplankton iron limitation in the Humboldt Current and Peru Upwelling. Limnology and Oceanography **47**: 997-1011.

Hutchins, D. A., P. N. Sedwick, G. R. DiTullio, P. W. Boyd, B. Quéguiner, F. B. Griffiths, and C. Crossley (2001). Control of phytoplankton growth by iron and silicic acid availability in the subantarctic Southern Ocean: Experimental results from the SAZ Project. Journal of Geophysical Research **106**: 31,559-31,572.

Koike, I., H. Ogawa, T. Nagata, R. Fukuda, and H. Fukuda (2001). Silicate to nitrate ratio of the upper sub-arctic Pacific and the Bering Sea basin in summer: Its implication for phytoplankton dynamics. Journal of Oceanography **57**: 253-260.

Landry, M. R., R. T. Barber, R. Bidigare, F. Chai, K. H. Coale, H. G. Dam, M. R. Lewis, S. T. Lindley, J. J. McCarthy, M. R. Roman, D. K. Stoecker, P. G. Verity, and J. R. White (1997). Iron and grazing constraints on primary production in the central equatorial Pacific: An EqPac synthesis. Limnology and Oceanography **42**: 405-418.

McRoy, C. P., T. E. Whitledge, A. M. Springer, and E. P. Simpson (2001). The nitrate front in the Bering Sea: Is this an iron curtain? Aquatic Sciences Meeting, Albuquerque, American Society of Limnology and Oceanography (Abstract).

Miller, C. B., B. W. Frost, B. Booth, P. A. Wheeler, M. R. Landry, and N. Welschmeyer (1991). Ecological processes in the subarctic Pacific: Iron limitation cannot be the whole story. Oceanography **4**: 71-78.

Morel, F. M. M., J. G. Rueter, and N. M. Price (1991). Iron nutrition of phytoplankton and its possible importance in the ecology of ocean regions with high nutrient and low biomass. Oceanography **4**: 56-61.

Parsons, T. R., Y. Maita, and C. M. Lalli (1984). A manual of chemical and biological methods for seawater analysis, Pergamon Press. 173 pp.

Price, N. M., B. A. Ahner, and M. M. Morel (1994). The equatorial Pacific Ocean: Grazer-controlled phytoplankton populations in an iron-limited ecosystem. Limnology and Oceanography **39**: 520-534.

Price, N. M., L. F. Andersen, and F. M. M. Morel (1991). Iron and nitrogen nutrition of equatorial Pacific plankton. Deep-Sea Research **38**: 1361-1378.

Sambrotto, R. N., H. J. Niebauer, J. J. Goering, and R. L. Iverson (1986). Relationships among vertical mixing, nitrate uptake, and phytoplankton growth during the spring bloom in the southeast Bering Sea middle shelf. Continental Shelf Research **5**: 161-198.

Shoaf, W. T. and B. W. Lium (1976). Improved extraction of chlorophyll-*a* and -*b* from algae using dimethyl sulfoxide. Limnology and Oceanography **21**: 926-928.

Slawyk, G., Y. Collos, and J. C. Auclair (1977). The use of the ^{13}C and ^{15}N isotopes for the simultaneous measurement of carbon and nitrogen turnover rates in marine phytoplankton. Limnology and Oceanography **22**: 925-932.

Springer, A. M., C. P. McRoy, and M. V. Flint (1996). The Bering Sea Green Belt: shelf-edge processes and ecosystem production. Fisheries Oceanography **5**: 205-223.

Takeda, S. (1998). Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. Nature **393**: 774-777.

Wheeler, P. A. and S. A. Kokkinakis (1990). Ammonium recycling limits nitrate use in the oceanic subarctic Pacific. Limnology and Oceanography **35**: 1267-1278.

Whitledge, T. E., W. S. Reeburgh, and J. J. Walsh (1986). Seasonal inorganic nitrogen distributions and dynamics in the southeastern Bering Sea. Continental Shelf Research **5**: 109-132.

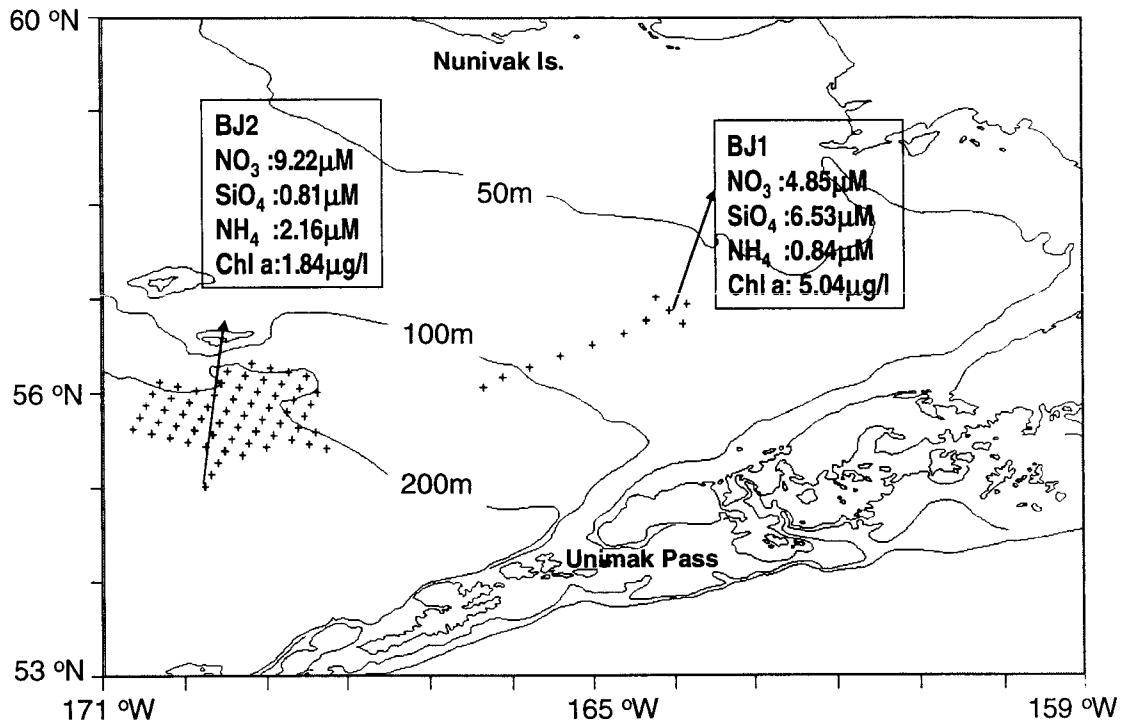

Fig.5.1. Water sampling locations for the shipboard Fe addition experiments over the middle shelf (BJ1) and in the open ocean region (BJ2) of the Bering Sea. Stations are marked with +)

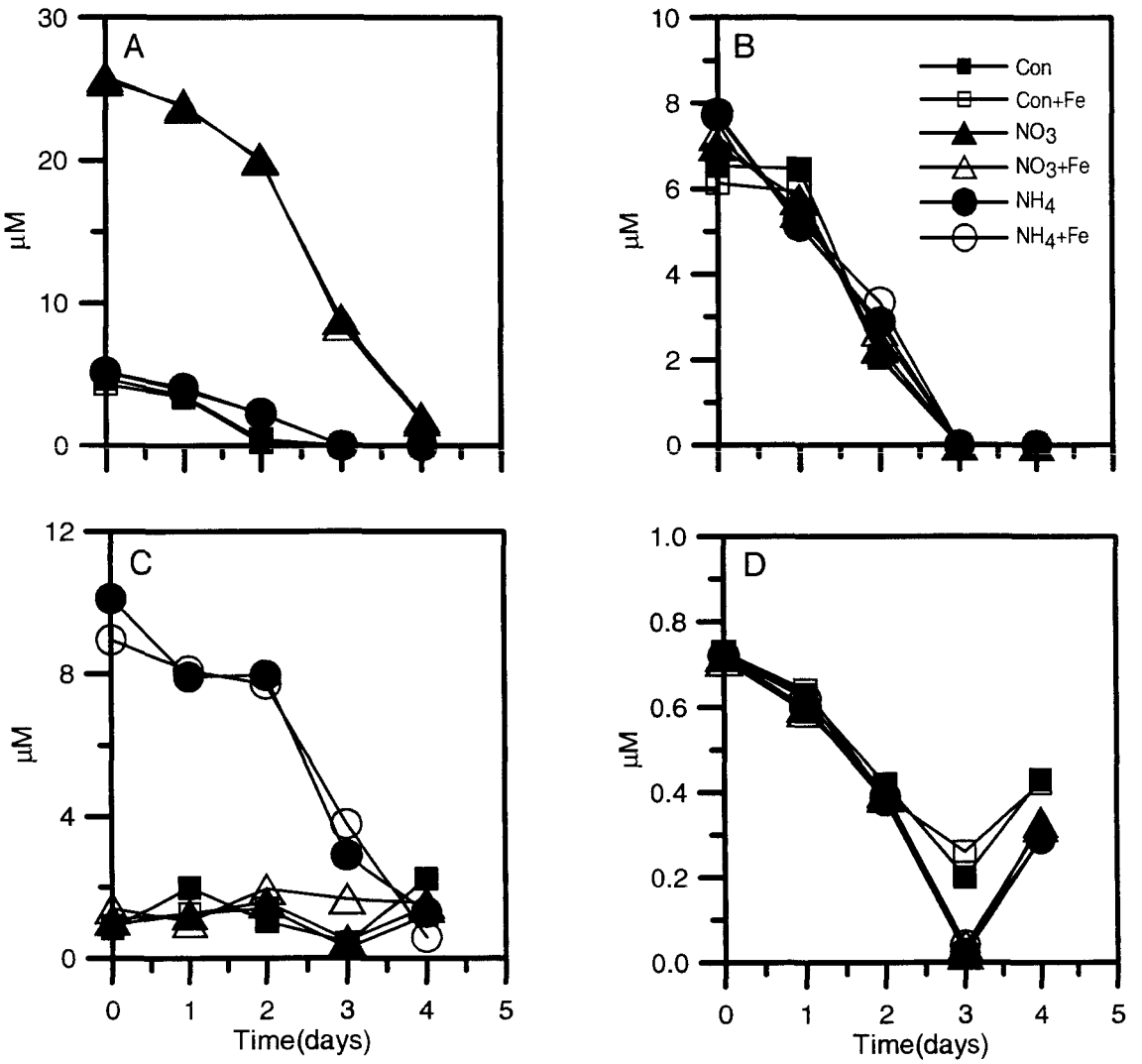

Fig.5.2. Variations of nutrient concentrations during the middle shelf experiment. A: nitrate, B: silicate, C: ammonium, and D: phosphate. In here, Con indicates control, Con+Fe indicates Fe addition, NO_3 indicates nitrate addition, NO_3+Fe indicates nitrate and Fe addition, NH_4 indicates ammonium addition, and NH_4+Fe indicates ammonium and Fe addition.

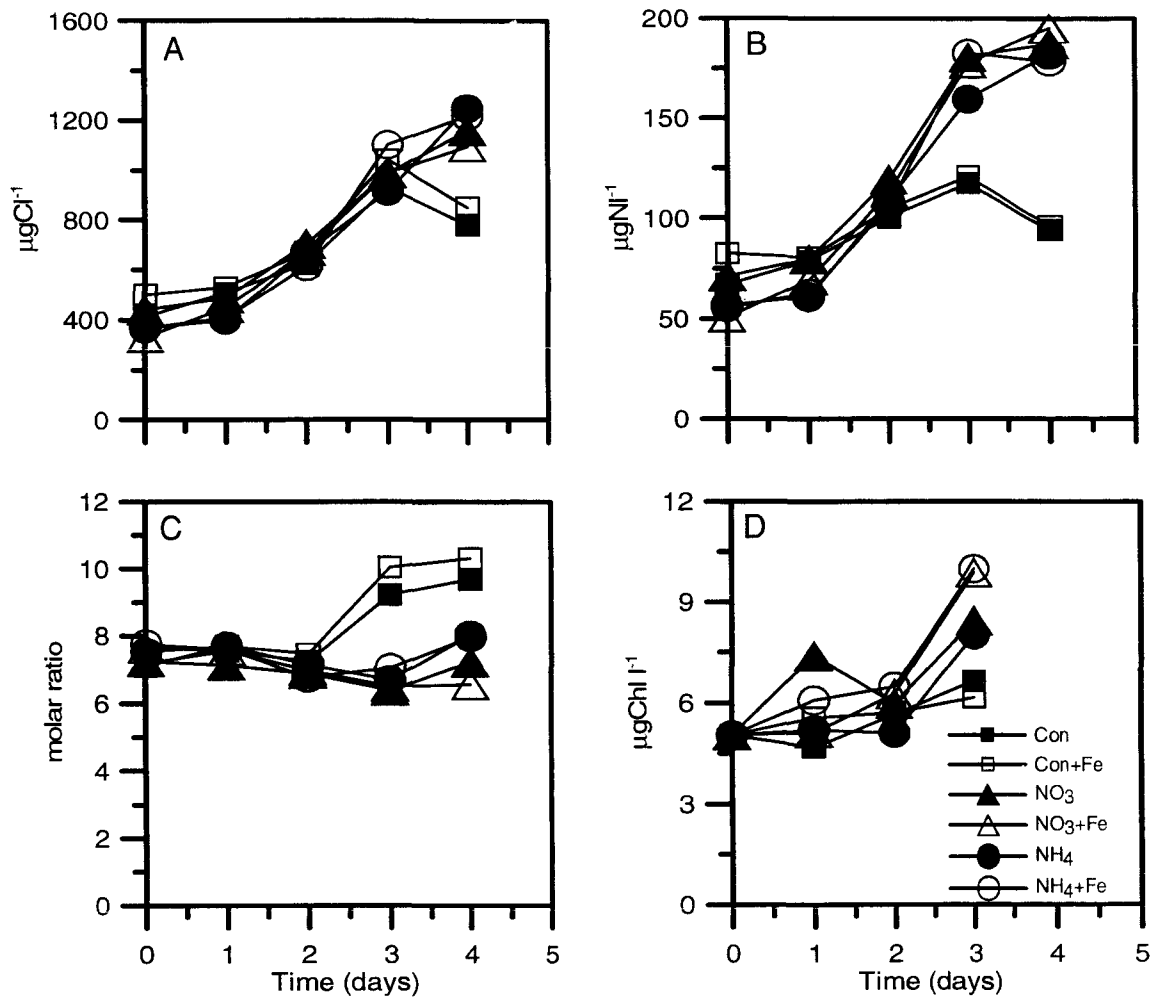

Fig.5.3. Variations of A: POC, B: PON, C: C:N ratio, and D: chlorophyll-*a* concentrations during the middle shelf experiment. In here, Con indicates control, Con+Fe indicates Fe addition, NO_3 indicates nitrate addition, NO_3+Fe indicates nitrate and Fe addition, NH_4 indicates ammonium addition, and NH_4+Fe indicates ammonium and Fe addition.

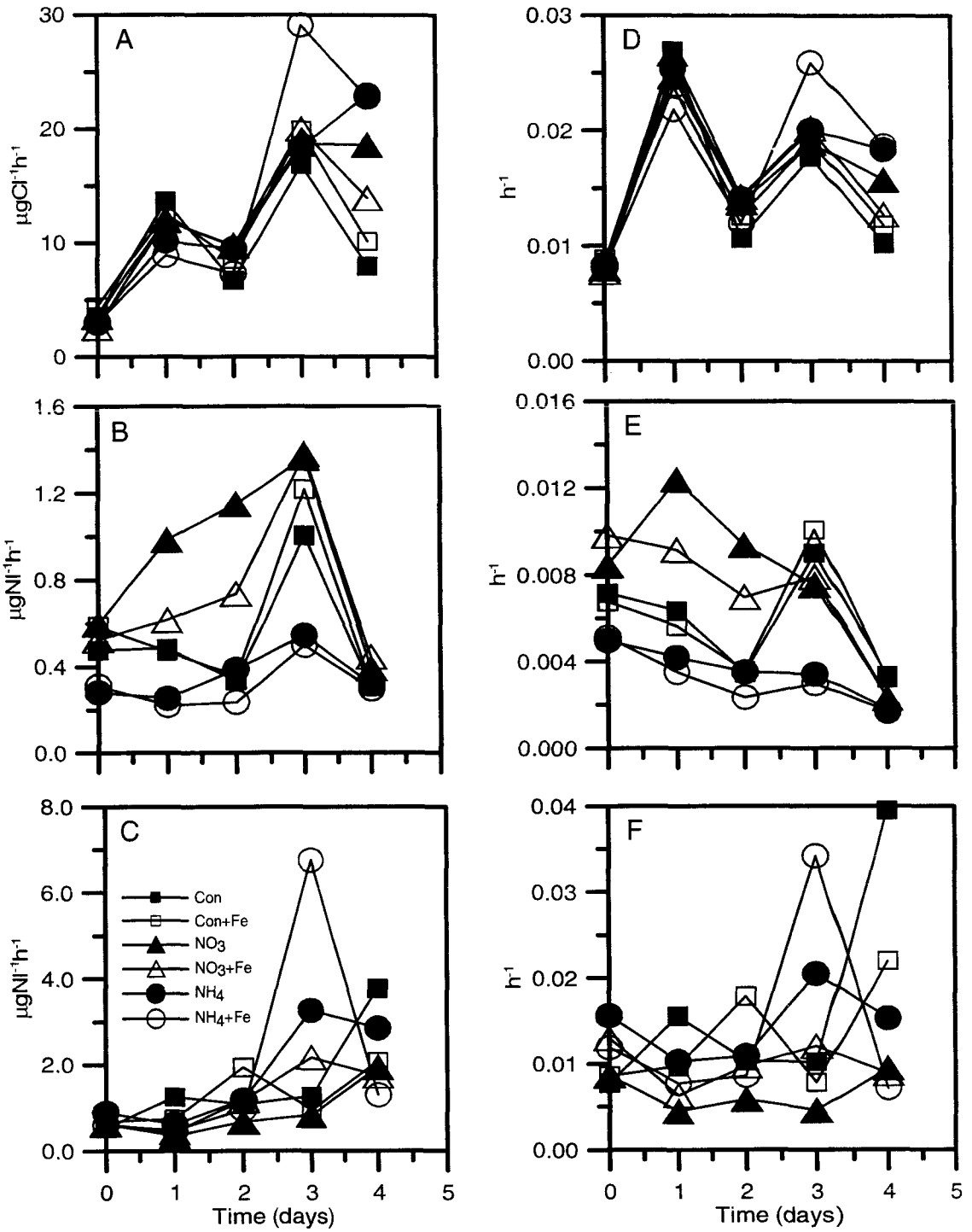

Fig.5.4. Variations of absolute uptake rates of A: carbon, B: nitrate, and C: ammonium and specific uptake rates of D: carbon, E: nitrate, and F: ammonium during the middle shelf experiments. In here, Con indicates control, Con+Fe indicates Fe addition, NO_3 indicates nitrate addition, NO_3+Fe indicates nitrate and Fe addition, NH_4 indicates ammonium addition, and NH_4+Fe indicates ammonium and Fe addition.

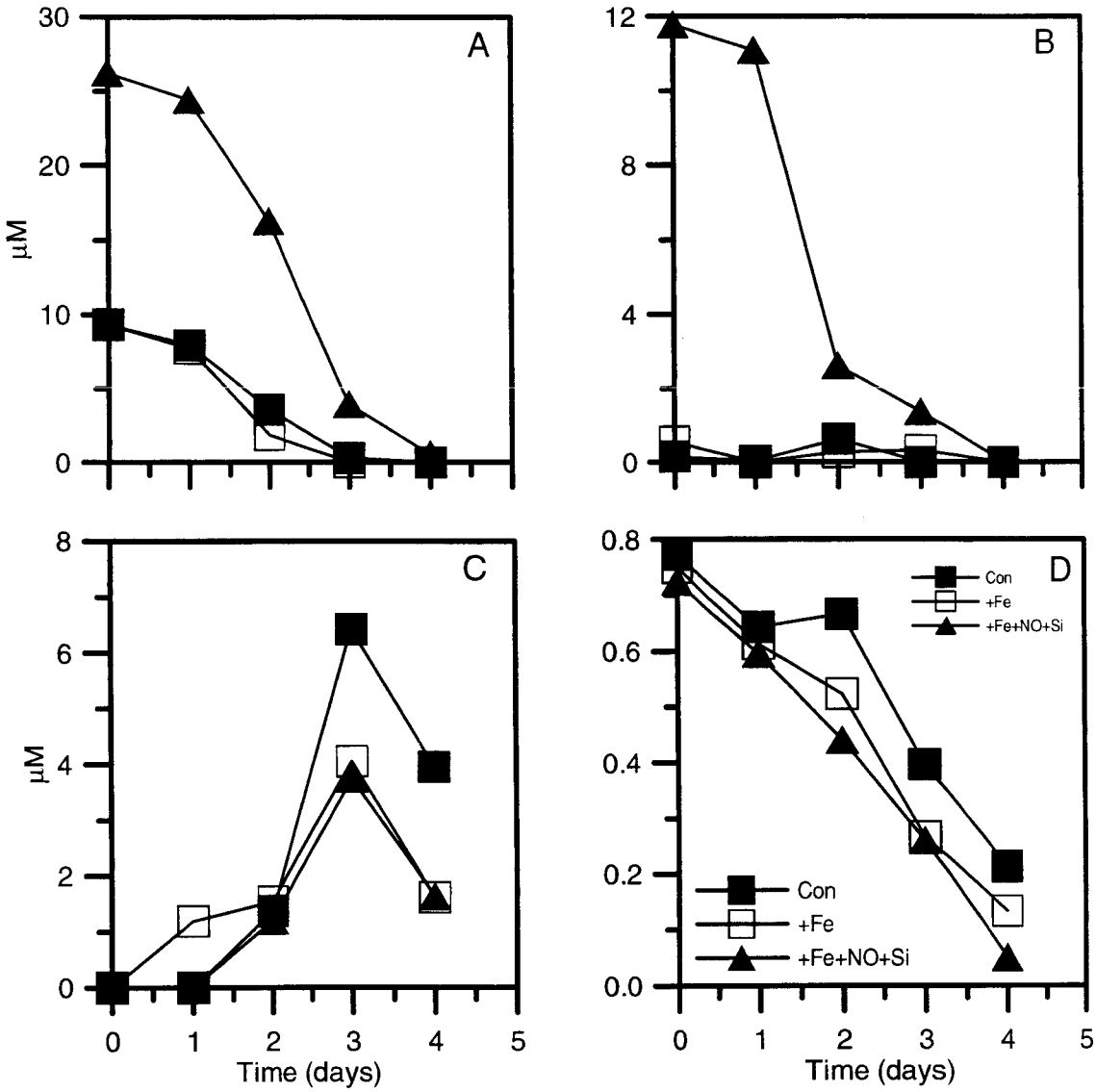

Fig.5.5. Changes of nutrient concentration during the open ocean experiment. A: nitrate, B: silicate, C: ammonium, and D: phosphate. In here, Con indicates control, +Fe indicates Fe addition, +Fe+NO+Si indicates Fe, nitrate, and silicate additions

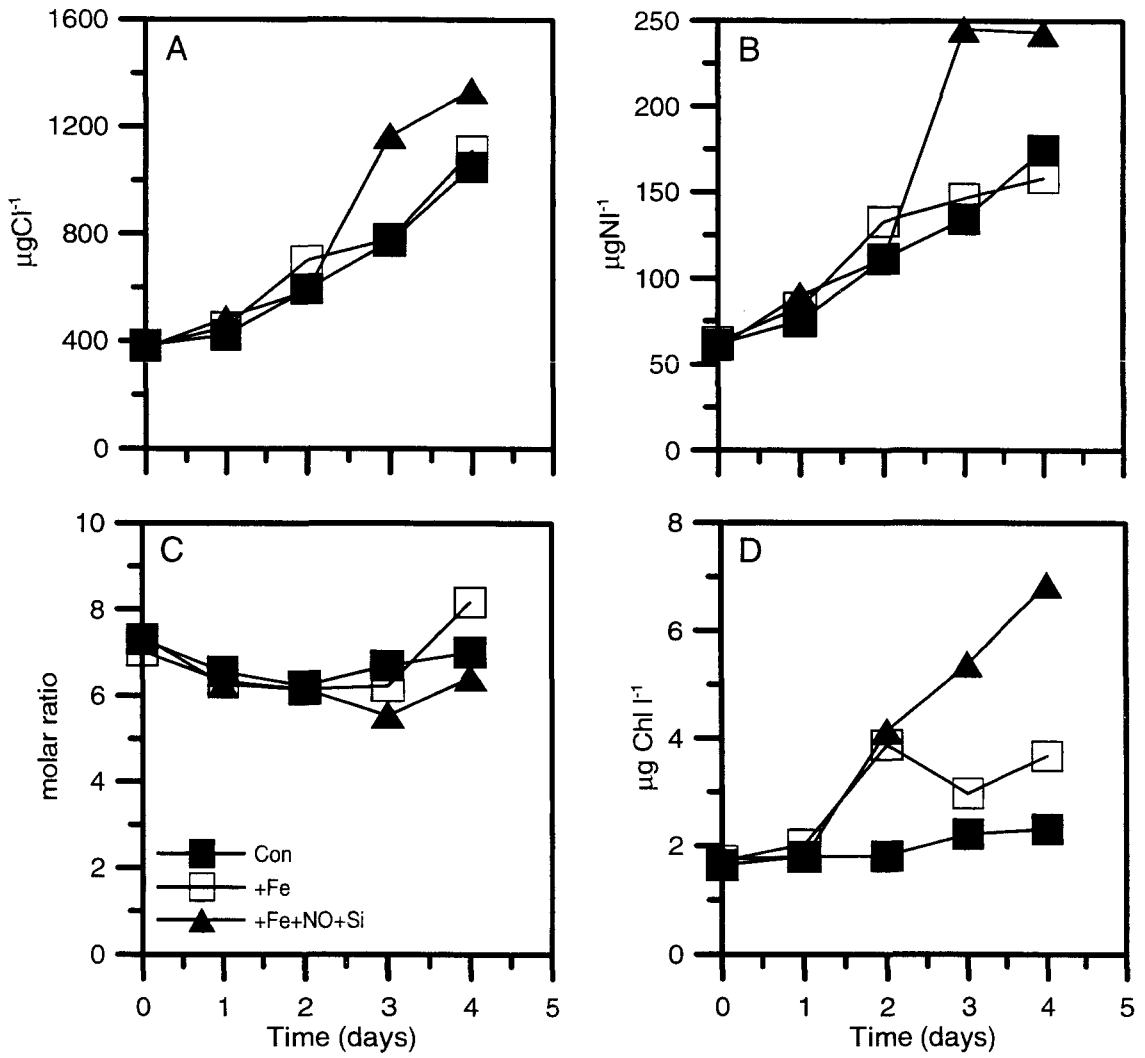

Fig.5.6. Variations of A: POC, B: PON, C: C:N ratio, and D: chlorophyll-*a* concentration during the open ocean experiment. In here, Con indicates control, +Fe indicates Fe addition, +Fe+NO+Si indicates Fe, nitrate, and silicate additions

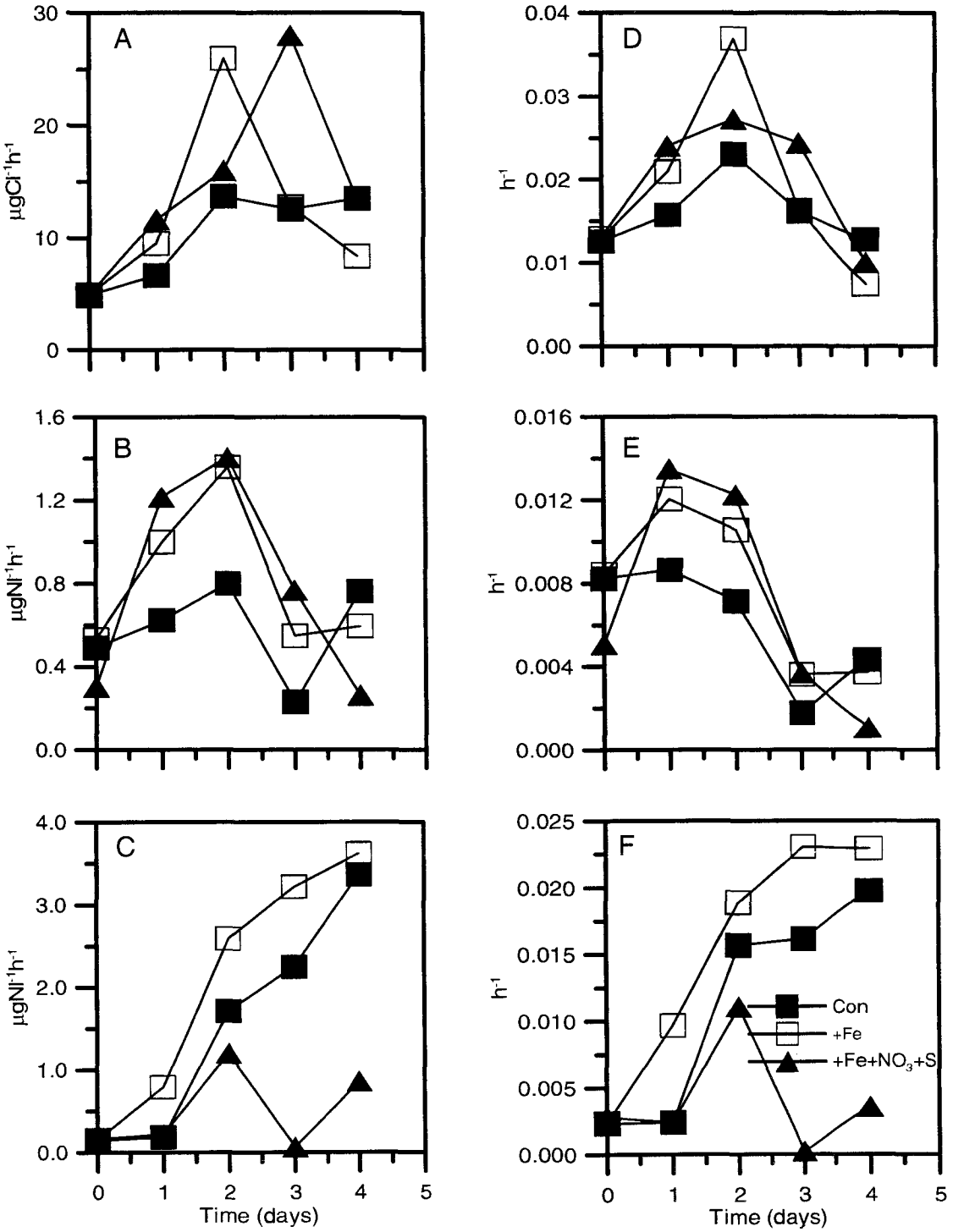

Fig.5.7. Variations of absolute uptake rates of A: carbon, B: nitrate, and C: ammonium and specific uptake rates of D: carbon, E: nitrate, and F: ammonium from the open ocean experiments. In here, Con indicates control, +Fe indicates Fe addition, +Fe+NO+Si indicates Fe, nitrate, and silicate additions

Table 5.1. Chlorophyll-*a* specific growth rates, nitrate consumption, POC and PON production, silicate consumption : chlorophyll-*a* increase, silicate: nitrate consumption ratio, and nitrate: phosphate consumption ratio for the middle shelf experiment. Chlorophyll-*a* growth rate, POC, and PON production, and nitrate consumption were estimated by subtraction of the initial value from day 3 value. Nitrate was depleted day 3. In here, Con indicates control, Con+Fe indicates Fe addition, NO_3 indicates nitrate addition, NO_3+Fe indicates nitrate and Fe addition, NH_4 indicates ammonium addition, and NH_4+Fe indicates ammonium and Fe addition.

Treatments		Chl Growth rate (d^{-1})	ΔNO_3^- (µmol/l)	Δ POC (µmol/l)	Δ PON (µmol/l)	Si:Chl-α (mol:g)	$Si:NO_3^-$ (mol:mol)	$NO_3^-:PO_4^{3-}$ (mol:mol)
Shelf (M2)	Con	0.5	4.7	43.1	4.2	10.8	1.4	8.9
	$+NO_3$	1.1	16.7	45.4	9.1	2.1	0.4	23.8
	$+NH_4$	1.0	5.2	45.8	8.6	2.6	1.5	7.4
	+Fe	0.4	4.3	45.1	3.2	5.5	1.4	9.2
	$+NO_3$+Fe	1.6	17.4	54.8	10.6	1.5	0.4	26.0
	$+NH_4$+Fe	1.6	5.2	61.0	10.6	1.6	1.5	7.6

Table 5.2. Chlorophyll-*a* specific growth rates, nitrate consumption, POC and PON production, silicate consumption : chlorophyll-*a* increase, silicate: nitrate consumption ratio, and nitrate: phosphate consumption ratio for the middle shelf experiment. Chlorophyll-*a* growth rate, POC, and PON production, and nitrate consumption were estimated by subtraction of the initial value from day 3 value. Nitrate was depleted day 3. In here, Con indicates control, +Fe indicates Fe addition, +Fe+NO+Si indicates Fe, nitrate, and silicate additions

Treatments	Growth rate (d^{-1})	ΔNO_3^- (µmol/l)	Δ POC (µmol/l)	Δ PON (µmol/l)	Si:Chl-α (mol:g)	$Si:NO_3^-$ (mol:mol)	$NO_3^-:PO_4^{3-}$ (mol:mol)
Con	0.2 ±0.24	9.3 ±0.08	55.3 ±5.78	9.4 ±0.81	0.1 ±0.13	0.01 ±0.01	16.6 ±0.17
+Fe	0.6 ±0.41	9.3 ±0.06	60.8 ±13.92	8.0 ±0.42	0.3 ±0.14	0.06 ±0.03	15.1 ±0.33
$+NO_3$+Si+Fe	1.7 ±0.30	25.7 ±0.73	80.0 ±4.60	15.3 ±0.59	2.3 ±0.11	0.46 ±0.01	38.1 ±0.12

Chapter 6. Nitrogen Dynamics of Summer Phytoplankton Over the Middle Domain of the Southeastern Bering Sea Shelf During 2000 and 2001

Abstract

Phytoplankton physiological changes in response to nutrient supplies to the nutrient-depleted surface euphotic by wind mixing after the spring phytoplankton bloom and the interactions between nitrate and ammonium, especially ammonium inhibition of nitrate uptake rates, were investigated using shipboard nutrient addition over the southeastern Bering Sea shelf middle shelf during summer 2000 and 2001. In general, nutrient concentrations decreased with time. However, silicate concentrations remained at constant levels in all treatments of most experiments, except for Experiment 2001-1. This suggests that the consumption of nutrients mainly resulted from non-diatom phytoplankton species. The enhancements of biomass and nitrogen uptake rates in response to nitrogen treatment suggest that the availability of nitrogen may be a primary controlling factor for phytoplankton over the middle shelf during summer. A large decrease in nitrate uptake rates occurred when ambient ammonium concentrations were high. Nitrate uptake rates increased as ambient ammonium concentrations decreased. This result suggests that external ammonium concentration played a very important role in nitrogen utilization. Carbon and nitrate uptake rates increased in response to the favorable light and nutrient conditions, similar to the 'shift-up' response of phytoplankton physiology in upwelling areas. However, the 'shift-up' response was less evident in the chlorophyll specific nitrate uptake rates when the proportion of detrital particulate nitrate concentration was high at the beginning of the experiment. This suggests that phytoplankton experienced a change of physiology due to the variation of environmental

conditions, but we have to be very careful in interpreting the result when the contribution of detrital particulate nitrogen to total particulate nitrogen was high.

Keywords: summer phytoplankton, ammonium inhibition, shift-up, nitrogen limitation, southeastern Bering Sea shelf

6.1. Introduction

The availability of nutrients is a very important controlling factor in the spatial distribution of primary production over the southeastern Bering Sea shelf (Sambrotto *et al.* 1986; Whitledge *et al.* 1986; Rho 2000), especially with respect to the amount of production and succession of phytoplankton species (Goering and Iverson 1981; Hansell *et al.* 1993). The seasonal cycle of nutrient concentrations was well described during the PROBES (Processes and Resources of the Bering Sea Shelf) study. Nutrients reach their maximum concentration in March just before the commencement of the spring phytoplankton bloom. They are depleted after the spring bloom within the surface euphotic layer, but high nitrate concentrations usually remain below the pycnocline (Whitledge *et al.* 1986).

After the establishment of a strong pycnocline, the supply of nutrients in the surface euphotic layer of the middle shelf is restricted by strong physical barriers such as the middle front (which slows horizontal advection and mixing) and the pycnocline (which inhibits vertical advection and mixing). However, strong winds, associated with a low pressure system, sometimes deepen the pycnocline and entrained nitrate rich water into the surface euphotic layer. During summer, high ammonium concentrations occur in the bottom layer of the middle shelf, due to decomposition of phytoplankton and/or benthic processes after the spring bloom (Whitledge *et al.* 1986). Thus, strong winds may also supply ammonium into the nutrient-depleted surface layer. Recent studies found high ammonium concentrations (7.5-8 μM) over most of the middle shelf during early spring (Rho 2000; chapter 2).

It is generally accepted that the growth of phytoplankton depends on the availability of nutrients and light. Thus, the supply of nutrients into the surface euphotic layer results in favorable light and nutrient conditions for the growth of phytoplankton. Previous studies have shown that the nitrate supplied by wind mixing enables continuous primary production during summer and increases new nitrogen production by approximately 37% in the middle domain of the southeastern Bering Sea shelf (Sambrotto *et al.* 1986; Whitledge *et al.* 1986). Whitledge *et al.* (1986) reported large accumulations of phytoplankton biomass as a result of nitrate enrichment by wind events. However, no studies have examined how phytoplankton respond to the wind-driven resupply of nutrients over the middle shelf of the southeastern Bering Sea. Changes in phytoplankton physiology have been studied in the upwelling regions off the coast of Peru, where the growth of phytoplankton in the newly upwelled water increased as they were exposed to the favorable light conditions, but subsequently decreased as nitrate concentrations were depleted in the surface layer (MacIsaac *et al.* 1985).

Concurrent high concentrations of nitrate and ammonium in early spring may cause complex interactions of nitrate and ammonium utilization. Many field and laboratory studies have been conducted to understand the mechanism of nitrate and ammonium interaction. It is known that ammonium and nitrate are important nitrogen sources for the growth of phytoplankton and ammonium is preferred over nitrogen even when nitrate is much more available (Collos and Slawyk 1980; McCarthy 1980; McCarthy 1981). Other studies showed that phytoplankton simultaneously utilized nitrate and ammonium in nitrogen-limited culture experiments (Bienfang 1975;

DeManche *et al.* 1979). The inhibition of nitrate uptake by ammonium was also observed in both culture (Eppley *et al.* 1969a; Cochlan and Harrison 1991) and field experiments (Wheeler and Kokkinakis 1990), although there is a contrary opinion that the inhibition by ammonium is not as common as generally assumed (Dortch 1990). However, no studies of the interaction between ammonium and nitrate utilization have been conducted in the southeastern Bering Sea.

This study was undertaken to understand which nutrients control primary production over the southeastern Bering Sea shelf during summer and how the phytoplankton respond to pulse inputs of nutrient rich water due to wind mixing events after the establishment of a strong pycnocline. We simulated the sporadic nutrient input into the euphotic layer by the addition of nitrate (20 μM), ammonium (20 μM), and silicate (20 μM) into clear 10L polycarbonate carboys and by incubating them under surface light levels.

6.2. Materials and Methods

6.2.1. Water collection light and shipboard incubations

Shipboard bioassay experiments to evaluate the effect of nitrate and ammonium additions on the carbon, nitrate and ammonium uptake rates were conducted over the middle shelf of the southeastern Bering Sea shelf (Fig. 6.1). Water for Experiment 2000-1 was collected in the upper-middle euphotic zone within the chlorophyll maximum depth interval (9-23m) on 03 July 2000 at a middle shelf station (M2 site, 56.87 °N 164.05 °W, 70m). For Experiment 2000-2, water was collected on 10 July 2000 from the M4 site in middle shelf (57.85 °N 167.87 °W, 70m), for Experiment 2001-1 water was

sampled on 16 August 20001 from the M4 site, and for Experiment 2001-2 water was sampled on 25 August 2001from a station north of M4 (58.75 °N 168.50 °W, 50m). All samples were collected using Niskin bottles mounted on a rosette sampler.

Water was transferred from the Niskin bottles through a 333μm screen to 10L polycarbonate containers. Then, six different nutrient treatments [control (Con), nitrate ($+NO_3^-$), ammonium ($+NH_4^+$), silicate ($+SiO_2$), and combined nitrate and silicate ($+NO_3^-$ $+SiO_2$)] were made. The specific treatments were selected from previous results of small volume nutrient amendment bioassay studies (Whitledge, unpublished data). For the nutrient treatments, stock solutions of nitrate, ammonium, and silicate (10mL of 20 μmol NO_3^-/ml and 20 μmol dissolved SiO_2/mL or 20 mL of 5 μmol NH_4^+/mL) were added into 10 L polycarbonate carboys to produce final concentrations of approximately 20 μM of nitrate and silicate and 10 μM of ammonium.

Incubation was conducted for 4-5 days in a deck incubator with running surface seawater under 100% of the ambient light level. During incubation, subsamples were taken daily from the 10L incubation carboys to measure nutrients, chlorophyll-*a*, POC, and PON concentrations. Carbon and nitrogen uptake rates were measured using $H^{13}CO_3^-$, $^{15}NO_3^-$, and $^{15}NH_4^+$ stable isotope techniques.

For small bottle nitrate and ammonium uptake experiment, water samples were taken from six depths, which corresponded to the 100, 50, 30, 12, 5, and 1% penetration of surface light, using a CTD/rosette sampler with 10L Niskin bottles and transferred to polycarbonate 1L incubation bottles that were covered with neutral density nickel or

stainless steel screens to simulate in situ light levels (i.e. 100, 50, 30, 12, 5, and 1%). Water samples were divided into four sets, which consist of six light levels. For nitrate uptake rates with varying nitrogen treatment, the water samples were inoculated with $H^{13}CO_3^-$ and $^{15}NO_3^-$ with four different nitrogen treatments [control, nitrate addition (1 mL of 10 µmole/mL NO_3^-), ammonium addition (1mL of 5µmole NH_4^+/mL), nitrate+ammonium addition (1 mL of 10 µmole NO_3^-/mL and 1mL of 5µmole NH_4^+/mL)]. For ammonium uptake rates with varying nitrogen treatment, the water samples were inoculated with $H^{13}CO_3^-$ and $^{15}NH_4^+$ with three different nitrogen treatments [control, nitrate addition (1 mL of 10 µmole NO_3^-/mL), ammonium addition (1mL of 5µmole NH_4^+/mL)]. Detailed description for incubation, analysis, and calculation Methods were found in the Materials and Methods section of chapter 2 and Rho (2000)

6.2.2. Nutrient analysis

The concentrations of nitrate, nitrite, ammonium, orthophosphate, and silicate were determined for all water samples on board according to the methods of Whitledge *et al.* (1981), using automated continuous flow analyzers.

6.2.3. Chlorophyll-*a* analysis

Subsamples (200-300ml) for chlorophyll analysis were taken daily and filtered on GF/F filters. The filters were kept in a freezer until the extraction of pigments using an acetone/DMSO procedure (Shoaf and Lium 1976). Concentrations of chlorophyll-*a* were determined fluorometrically using a Turner Designs Model 10-005RU Fluorometer (Parsons *et al.* 1984).

6.2.4. Carbon and nitrogen uptake rates

Subsamples for carbon and nitrogen uptake were taken and transferred to polycarbonate bottles (300mL), which were inoculated according to a double labeling technique (Slawyk *et al.* 1977). The incubation bottles were placed in an on-deck incubator with circulating surface seawater for 4 hr. The samples were filtered through precombusted (at 450° C for 4hr) GF/F filters and were kept frozen until analysis in the Fairbanks laboratory.

6.2.5. POC, PON, and isotope analysis

In the laboratory, the filters were fumed with concentrated hydrochloric acid to remove inorganic carbon, and were subsequently dried at 60° C for 24 hr. Isotope ratios, POC and PON concentrations of the samples were analyzed using a Finnigan Delta+XL IRMS. The equation of Dugdale and Goering (1967) was used to calculate carbon and nitrogen uptake rates. The isotopic dilution effect was not included in the uptake calculation because of the short incubations (Glibert *et al.* 1982).

6.3. Results

6.3.1. Nutrient dynamics

Initial nitrate concentrations ranged from 0.1 to 5.2 μM among the different experiments. Nitrate concentrations showed large variations with time, but the variations were slightly different depending on the initial nitrate concentrations and the addition of different nutrient combinations (Fig.6.2). In the nitrate treatment, nitrate concentrations generally showed a large decrease with time, and were depleted by day 4 in Experiment 2001-1. In the other experiments, however, nitrate was still not depleted between day 6 and day 8. Nitrate consumption rates were low at the beginning of experiment and

showed a rapid decrease between day 4 and day 6. Nitrate consumption rates were not affected by silicate addition during the summer 2000 experiments, but were slightly enhanced in $+NO_3^-+SiO_2$ treatments, compared with the nitrate treatment alone, during the summer 2001 experiments. Nitrate consumption rates also changed when ammonium was added (Fig.6.2). In Experiment 2000-1, ambient nitrate concentrations (5.2 μM) were consumed within 2 days in the control and $+SiO_2$ treatments. For the $+NH_4^+$ and $+NH_4+SiO_2$ treatments in the same experiment, however, nitrate was not completely utilized on day 2, and was consumed rapidly between day 3 and day 4, when ammonium concentrations fell below ca. 3-7 μM.

Ambient ammonium concentrations ranged from 0.66 to 2.73 μM, and showed different variations with time in the different experiments (Fig.6.2). Ambient ammonium concentrations were depleted within 2 days during the 2001 experiments. However, they generally remained at constant levels during the 2000 experiments. In general, ammonium concentrations in the $+NH_4^+$ and $+NH_4^++SiO_2$ treatments decreased rapidly with time, but were still not depleted at the end of experiments. The effects of silicate addition on the ammonium consumption were variable. Ammonium consumption increased with silicate addition in Experiment 2000-1 and Experiment 2001-2, was unchanged in Experiment 2000-2, and decreased in Experiment 2001-1.

Ambient phosphate concentrations ranged from 0.27 to 1.15 μM, and varied with time in all treatments (Fig.6.2). In general, the consumption of phosphate was much higher with the nitrogen treatments than without. In Experiment 2000-1, the consumption of phosphate was much faster with the ammonium treatment than with the

nitrate treatment (Fig.6.2). There was no apparent difference in phosphate consumption due to silicate addition in any of the experiments.

Ambient silicate concentrations ranged from 1.05 to 18.55 μM, and remained at an almost constant level with time in most of the experiments (Fig.6.2). For the $+NH_4^+ + SiO_2$ and $+NO_3^- + SiO_2$ treatments of Experiment 2001-2, silicate concentrations showed a large decrease after day 3, while relatively constant levels occurred with the addition of silicate alone.

6.3.2. Biomass

Ambient chlorophyll-*a* concentrations varied from 0.25-3.62 mg chl-*a* m^{-3}. In all experiments, chlorophyll-*a* concentrations were enhanced by the nitrogen treatments, and decreased after nitrogen was depleted, but the chlorophyll-*a* remained at almost constant levels with time in the control and $+SiO_2$ treatments (Fig.6.3). In the summer 2000 experiments the increases in chlorophyll-*a* were slightly faster and the maximum chlorophyll-*a* concentrations were slightly higher in the ammonium treatments than in the nitrate treatments. Addition of both silicate and nitrogen resulted in greater chlorophyll-*a* increase rates and maximum values for Experiment 2001-2, but silicate addition had no effect in other experiments (Fig.6.3).

POC and PON concentrations in all experiments showed trends similar to that of chlorophyll-*a* (Fig.6.3). Unlike chlorophyll-*a* concentrations, POC and PON concentrations did not show large decreases toward the end of the experiment, except a slight decrease of PON in Experiment 2000-1. The initial C:N ratios of particulate organic materials varied from 6.34 to 11.7, and were greater during late August 2001 than

during early July 2000. In general, C:N ratios decreased with time in the nitrogen treatments, while they remained at a constant level or showed a slight increase in the control and silicate only treatments. In Experiment 2000-1, however, C:N ratios in all treatments gradually increased with time.

The initial PN:Chl-*a* ratios were typically between 1.25 and 1.94 (mg at N: mg chl-*a*) in most experiments. However, in Experiment 200-2, the initial PN: Chl-*a* ratios ranged from 2.9 to 4.0 (Fig.6. 4). This suggests that there were large proportions of detrital particulate nitrogen (Garside 1991). PN:Chl-a ratios generally increased with time in the control and silicate only treatments, but remained constant or decreased in nitrogen treatments. In Experiment 2001-2, PN:Chl-*a* ratios for the nitrogen treatments decreased below 1:1, indicating a healthy phytoplankton population (Garside 1991).

6.3.3. Carbon uptake rates

In all experiments, absolute carbon uptake rates showed little change with time in the control and silicate only treatments. In the other treatments, carbon uptake rates showed a large increase between day 2 and day 4 and a rapid decrease toward the end of each experiment (Fig.6. 5). During Experiment 2000-1, the slope of uptake rates was steeper, and the maximum value of absolute carbon uptake was greater, in the ammonium treatments than in the nitrate treatments. This is also clearly reflected in the chlorophyll-*a*, POC, and PON concentrations (Fig.6.3). However, in other experiments, there were no systematic changes in the slope of uptake rates and the maximum value of absolute carbon uptake due to different nitrogen treatment. In general, there was no difference in absolute carbon uptake rates due to the silicate treatment. However, in Experiment 2001-

2, absolute carbon uptake rates were enhanced by silicate+nitrogen treatments, although silicate treatment alone did not have any effect (Fig.6.5). In general, the trends of biomass specific carbon uptake rate were similar to those of absolute carbon uptake rates, regardless of normalization to particulate carbon or chlorophyll-*a* concentrations (Fig.6.5).

6.3.4. Nitrate uptake rates

Absolute nitrate uptake rates increased rapidly in response to nitrate treatments until day 2 or day 3, and then decreased sharply as nitrate concentrations were depleted. When no nitrate was added, however, absolute nitrate uptake rates remained at low levels throughout the experiments (Fig.6.6). Absolute nitrate uptake rates were lower in the ammonium treatments than in the control or silicate only treatments. In Experiment 2000-1, absolute nitrate uptake rates decreased in the ammonium treatment until day 2, when ammonium concentrations were high, and increased slightly after ammonium was depleted. In Experiment 2001-2, absolute nitrate uptake rates were slightly higher in the $+NO_3^+ + SiO_2$ treatment than in the $+NO_3^+$ treatment. Biomass specific nitrate uptake rates showed trends similar to those of absolute nitrate uptake rates. The relative increases in PN specific nitrate uptake rates were generally lower than those of chlorophyll-*a* specific uptake rates.

6.3.5. Ammonium uptake rates

Absolute ammonium uptake rates were enhanced by the ammonium treatment in both 2001 experiments, but were not enhanced in either experiment in 2000. An enhancement of ammonium uptake rates was observed in the $+NH_4^+ + SiO_2$ treatment

compared with in the + NH_4^+ treatment for Experiment 2001-2 (Fig.6.7). In general, biomass specific uptake rates showed a trend similar to that of absolute uptake rates, and chlorophyll-*a* and PN specific ammonium uptake rates were similar in most experiments. However, in Experiment 2000-2, ammonium uptake rates were lower in the ammonium treatments compared to other treatments.

6.3.6. The effects of nitrate and ammonium addition on nitrate and ammonium uptake rates

During summer of 2000, PN specific nitrate uptake rates were greatly enhanced by nitrate addition and greatly reduced by ammonium addition, at 12 to 100% of the surface light level (Fig.6.8). For the combined addition of nitrate and ammonium, PN specific nitrate uptake rates were lower than those for the control and nitrate only addition, but were slightly higher than those for the ammonium addition. However, they were not affected by the nitrate and/or ammonium additions at 1 to 5% of surface light. PN specific ammonium uptake rates were reduced by the nitrate and/or ammonium additions at 30 to 100% of the surface light level, but were not affected below 12% surface light levels (Fig.6.9). PN specific ammonium uptake rates were slightly higher in the nitrate treatment than in the ammonium treatment at light level between 50 and 100%. Although there were large variations of PN specific nitrate and ammonium uptake rates, PC specific carbon uptake rates were generally not affected by different nutrient treatments (Fig.6.8; Fig.6.9)

6.4. Discussion

6.4.1. Summer phytoplankton composition

Over the southeastern Bering Sea shelf, phytoplankton undergoes seasonal succession of community composition which has been described in terms of three assemblages, stage-I, stage-II, and stage-III group (Goering and Iverson 1981). Succession occurs in response to changes in the availability of light and nutrients and selective grazing on specific species. When nutrient concentrations are depleted in the surface euphotic layer, the stage-II community is replaced by the stage-III phytoplankton group, which is able to grow under low nutrient concentrations and is dominated by *Rhizosolenia alata* (Goering and Iverson 1981). Our results show that phytoplankton utilized added nitrate and ammonium, but silicate was not consumed in most experiments, which suggest that the phytoplankton community may be dominated by non diatom species at the beginning of most experiments (Fig.6.2). In Experiment 2001-2, however, silicate concentrations decreased with time in nitrogen treatments, while silicate concentrations were maintained at constant levels without nitrogen addition, suggesting that the proportion of diatoms in the phytoplankton community may have been greater than in the other experiments. Size fractionated chlorophyll-*a* concentrations over the middle shelf of southeastern Bering Sea in August 2001 showed that small phytoplankton (< 10 um) were dominant in the surface layer or chlorophyll-*a* maximum layer (81-100% of total) (Lessard *et al.* 2002).

6.4.2. Nitrogen limitation of phytoplankton growth during summer

The variations of phytoplankton biomass with time, represented by chlorophyll-*a*, POC, and PON concentrations, clearly show that the growth of phytoplankton was

enhanced by the nitrogen treatments (Fig.6.3). The maximum values of phytoplankton biomass in each experiment were not affected by the nitrogen source (nitrate or ammonium). Phytoplankton utilized most of the nitrate or ammonium added within 4-8 days (Fig.6.2). Chlorophyll-*a* concentrations were especially sensitive to nutrient depletion compared to POC and PON concentrations. Chlorophyll-*a* concentrations increased with nitrogen additions and then decreased rapidly as added nitrogen concentrations were depleted, while POC and PON concentrations remained the same or decreased slightly. The variations of POC and PON concentrations were probably the net result of nearly equal production and the remineralization of particulate organic material, but chlorophyll-*a* concentrations can be altered by production, remineralization, and decreases in chlorophyll-*a* content per cell due to nutrient limitation (Kudela and Dugdale 2000, and references therein).

Carbon and nitrate uptake rates demonstrated that the enhancement of biomass by nitrogen addition is probably not the result of the accumulation of biomass due to the lack of grazing, since carbon uptake rates increased due to the favorable nitrogen conditions. The enhancement of carbon uptake rates was very similar in both the nitrate and ammonium treatments in most experiments. In the 2000 experiments, however, carbon uptake rates were slightly greater in the ammonium treatment, than in the nitrate treatment although maximum uptake rates were similar in both treatments (Fig.6.4; Fig.6.5; Fig.6.7).

The addition of silicate showed no apparent effects on the phytoplankton biomass and carbon and nitrogen uptake rates in most experiments (Fig.6.3; Fig.6.4; Fig.6.5;

Fig.6.7). In Experiment 2001-2, however, biomass increased more due to the combined addition of nitrogen and silicate compared to the addition of nitrate or ammonium alone (Fig.6.3). Variations of nutrient concentrations corresponded to the trends in biomass. The consumption of nitrate and ammonium was enhanced by silicate addition (Fig.6.2). Carbon, nitrate, and ammonium uptake rates were also greater with the combined addition of nitrogen and silicate than with the addition of nitrate or ammonium alone (Fig.6.4; Fig.6.5; Fig.6.7). However, these trends were not observed for the addition of silicate alone. This suggests that the growth of phytoplankton was primarily limited by the availability of nitrogen, and that silicate may be a secondary controlling factor, which can modify the growth of phytoplankton in nitrogen replete conditions. Kudela and Dugdale (2000) also demonstrated that silicate was not directly a limiting factor for phytoplankton growth, but could modify nitrate uptake rates in Monterey Bay, California.

6.4.3. Dynamics of nitrate and ammonium utilization

Various mechanisms have been proposed to understand the inhibition of phytoplankton nitrate uptake by ammonium and their preference for ammonium. A relationship between external ammonium concentrations and nitrate uptake rates indicated that external ammonium concentrations are directly responsible for the ammonium inhibition of nitrate uptake rates (Dugdale 1976; McCarthy 1981). External ammonium may compete with nitrate for the ATP energy used to transport ammonium into the cell (Bates 1976) or for its assimilation into amino acids by glutamine synthetase (Ohmori *et al.* 1977). The inhibition of ammonium uptake by nitrate and constant total

nitrogen uptake rates indicate a competitive interaction between nitrate and ammonium (Dortch and Conway 1984), which should result in a gradual increase of nitrate uptake rates as ammonium uptake rates decrease. Dortch and Conway (1984), however, observed that the nitrate uptake rate did not increase until very low ammonium concentrations were achieved, which suggested the possibility of non-competitive inhibition (Zevenboom and Mur 1981).

The degree of ammonium inhibition of nitrate uptake depends on the preconditioning growth rate. Also, nitrogen source and ammonium inhibition of nitrate uptake can continue after the depletion of ammonium in *Skeletonema costatum* cultures (Dortch and Conway 1984). This evidence suggests that it is very hard to explain the ammonium inhibition of nitrate uptake based upon external ammonium concentration alone. Other studies have suggested that the effect of ammonium on nitrate uptake rates may be related to the accumulation of internal nitrogen compounds, such as ammonium (DeManche *et al.* 1979), organic end products of ammonium assimilation (Syrett 1981), total amino acids (Conway 1977), and dissolved organic nitrogen (DeManche *et al.* 1979). DeManche *et al.* (1979) found that rapid nitrate uptake occurred when phytoplankton were exposed to both nitrate and ammonium, but nitrate consumption did not occur until internal ammonium concentrations were depleted. They also found that nitrate uptake rates were most rapid when external ammonium concentrations were maximal.

The preference for ammonium was known to result from an energetic advantage (Eppley *et al.* 1969a; Dortch *et al.* 1982; Horrigan and McCarthy 1982). Thus, a greater

inhibition of nitrate uptake by ammonium is expected under low irradiance than under high irradiance. However, our results showed that the ammonium inhibition on nitrate uptake rate was high in the surface layer (> 12% of surface light intensities), while there was no apparent difference in nitrate uptake rates between the control and ammonium treatments at 20m and greater depths (Fig.6.8). The marine diatom, *Thalassiosira pseudonana*, grown under light-limited conditions, showed no significant differences in growth rates between nitrate-grown cells and ammonium-grown cells (Thompson *et al.* 1989). Yin *et al.* (1998) found that there was a significant inhibition of nitrate uptake rates by ammonium in a nitrate-saturated experiment, while no inhibition was observed in light-limited experiments. These results suggest that the preference for ammonium or the inhibition of nitrate uptake by ammonium cannot be simply explained by the energetic advantage of ammonium uptake over nitrate uptake.

It was believed that nitrate uptake rates were controlled by the reduction rate of nitrate, because of tight coupling between nitrate uptake and reduction (Butz and Jackson 1977). The reduction of nitrate requires an enzyme called nitrate reductase (NR). The synthesis of the enzyme is induced by nitrate and is repressed in the presence of high external ammonium concentrations (Eppley *et al.* 1969a; Syrett and Leftley 1976). Dortch and Ahmed (1979) showed that that the repression of NR activity was not directly related to external ammonium, but resulted from a product of ammonium assimilation, and that the repression of NR activity by ammonium varied with the nitrogen source of the culture during a pre-conditioning period. Dortch (1982) reported the accumulation of internal nitrate pools after the addition of nitrate to nitrogen-deficient or nitrogen-starved

cultures of *S. costatum*, which suggested that the assimilation of nitrate is slower than nitrate uptake, so that nitrate assimilation may be the rate limiting step for nitrate utilization. This also confirmed the early hypothesis that NR synthesis was induced by the internal nitrate pools rather than the external nitrate pools (Dortch and Ahmed 1979). The size and the accumulation rate of the internal nitrate pool were affected by the nitrogen sources or supply rate during pre-conditioning, but the size and accumulation rate of internal ammonium pools showed little variation due to preconditioning, except for severely nitrogen depleted conditions (Dortch 1982). Some evidence indicates the inhibition of nitrate uptake may not result from the internal ammonium pools. Dortch and Conway (1984) reported that there were large variations of internal ammonium concentrations at the time that external ammonium was depleted and nitrate uptake rates increased significantly. Some phytoplankton species, such as *Chaetoceros debilis*, showed strong inhibition of nitrate uptake rates by ammonium although no accumulation of internal ammonium pools was observed under any circumstances (Dortch 1982).

Our Bering Sea study does not provide clear answers to the question of how and what inhibits nitrate uptake rates. The results of our study indicate that the interaction between nitrate and ammonium was closely related to external ammonium concentration, and that the interaction rather non-competitive inhibition was more important. Specific nitrate uptake rates were inhibited by high external ammonium concentrations, but increased to rates similar to the maximum rate in the control as soon as external ammonium concentrations decreased below 3-7 μM (Fig.6.2; Fig.6.6). The instant increase of nitrate specific uptake rates when external ammonium concentration reached

threshold values (3-7 μM) suggests that the potential for nitrate uptake was not eliminated by the presence of high ammonium. Other experiments in this study also showed an increase of specific nitrate uptake rates due to nitrate addition without any lag period, which suggested that phytoplankton still had the ability to utilize nitrate (Fig.6.2). In the small bottle ammonium inhibition experiment, phytoplankton still utilized nitrate in the ammonium treatment and after simultaneous treatment with nitrate and ammonium, although nitrate specific uptake rates decreased greatly compared with those for the control and nitrate addition alone. This could be due to the constant levels of total nitrate reductase activity per unit volume, although activity per unit chlorophyll-*a* declined (Holmes *et al.* 1966). Thus, our results support the hypothesis that ammonium and products of ammonium assimilation do not repress the capacity of nitrate uptake, although they inhibit nitrate uptake (Dortch and Conway 1984). However, an increase of nitrate specific uptake rates did not occur until day 3 in the nitrate addition experiments and then they increased rapidly, which suggests that induction of the ability to utilize nitrate was required.

The carbon uptake rate of phytoplankton was not changed by the combined addition of nitrate and ammonium, although nitrate uptake rates were greatly inhibited by ammonium. Our results showed that maximum carbon specific uptake rates showed very similar values in both the nitrate and ammonium treatments in the large bottle incubations (Fig.6.5). In the small bottle ammonium inhibition experiments carbon specific uptake rates were almost same as those in the control for all nitrogen additions, despite of large variations in nitrate specific uptake rates (Fig.6.8; Fig.6.9). In general, the threshold

ammonium concentrations for inhibition of nitrate uptake are known to be on the order of 1 μM (Conway 1977; McCarthy 1981). However, there were large variations in the threshold values observed in different studies. Wheeler and Kokkinakis (1990) measured very low ammonium threshold values (0.1-0.3 μM) in the oceanic subarctic Pacific. Cochlan and Harrison (1991) observed complete inhibition of nitrate uptake in the range of 1-10 μM ammonium in nitrate-replete cultures of the picoflagellate *Micromonas pusilla*. Dortch (1990) compiled a wide range of ammonium threshold values for nitrate inhibition from the literature. The threshold values ranged from 0.1 to 90 μM in culture experiments and from 0.1 to 15 μM in field measurements. In this study, specific nitrate uptake rates clearly showed that nitrate uptake rates increased and reached the same uptake rates as the control treatment after ammonium concentrations decreased to threshold values (3-7 μM). Although the interacting biochemical processes are currently unknown, our threshold values (3-7 μM) were within the range of field values from other studies. The suppression of nitrate uptake rates by ammonium varied with the dominant phytoplankton species, previous nitrogen exposure, and the degree of nitrogen deficiency (Conway 1977; Dortch and Conway 1984). Thus, it may be unrealistic to expect the same threshold value of ammonium concentrations for the inhibition of nitrate uptake with different environmental conditions and phytoplankton species assemblages.

6.4.4. Physiological adaptations in response to changing conditions

A 'shift-up' hypothesis, which could explain changing maximal nutrient uptake rates observed in the field data, was introduced by MacIsaac *et al.* (1985) to describe the productivity of phytoplankton in an upwelling area off the coast of Peru. They observed

four zones of physiological adaptations due to varying light and nutrient conditions along the axis of the upwelling plume. Phytoplankton in the recently upwelled water are 'shifted-down' (i.e. low V_{max}) due to unfavorable light conditions at depth, in spite of high nutrient concentrations (Stage-I). After upwelling, phytoplankton 'shift-up' to increase nutrient uptake, photosynthesis, and synthesis of macromolecules in response to the favorable surface light conditions (Stage-II). This resulted in a rapid decrease of nutrient concentrations and a rapid accumulation of phytoplankton biomass in the water column, and the highest growth rate of phytoplankton (Stage-III). As nutrient concentrations were depleted, phytoplankton underwent 'shift-down' to lower rates of nutrient uptake, photosynthesis, and macromolecule synthesis (Stage-IV). These physiological changes occurred in a very short time period (8-10 days) and a narrow spatial domain (30 to 60 km off the coast). In further studies, using large shipboard barrels and Lagrangian sampling following upwelled water with drifters (Wilkerson and Dugdale 1987), and a modeling analysis (Zimmerman *et al.* 1987), it was confirmed that the shift-up and shift-down of maximal nitrate uptake rate occurred due to the changes in light and nutrient conditions.

In this study, as explained in the Materials and Methods section, we collected the water at the chlorophyll maximum (9-23m) and incubated it under surface light conditions, which is similar to an upwelling simulation. There was no apparent 'shift-up' physiological change in the control treatment of most experiments, probably due to the low nitrate concentration. However, the acceleration of nitrate specific uptake rates occurred in the control of Experiment 2000-1, which had about 5 μM of nitrate at the

beginning (Fig.6.2; Fig.6.6). Biomass specific uptake rates decreased as nitrate concentrations were depleted after day 2. The increase of specific nitrate uptake was more evident in the nitrate treatment of Experiment 2000-1. Our experiments showed that biomass specific nitrate uptake rates increased due to favorable environmental conditions, such as the availability of nutrients and light, and decreased when nutrients were depleted. This was very similar to the 'shift-up' adjustment of phytoplankton physiology in the upwelling system (MacIsaac *et al.* 1985; Wilkerson and Dugdale 1987; Zimmerman *et al.* 1987; Kudela and Dugdale 2000).

In a model study, Garside (1991) showed that there was no shift-up response when the initial nitrate concentration was below a critical value (1-2 μM), and that the acceleration of specific nitrate uptake rates and the time to maximum specific uptake rates both increased as the initial nitrate concentration increased. In our Bering Sea experiments, there were no increase of nitrate uptake rates in the control and silicate only treatments of most experiments, which had initial nitrate concentrations less than 2 μM, except for Experiment 2000-1. In that experiment, the slope of the biomass specific nitrate uptake rates was similar in both the control and the nitrate treatments, and the maximum rate was reached at the same time, although the maximum rate was higher in the nitrate treatment than in the control (Fig.6.2; Fig.6.6). Our results agreed well with the model result of no shift-up response at low initial nitrate concentrations. However, our results did not show that the increased acceleration of specific nitrate uptake rates and the change of timing for maximum specific nitrate uptake rates depended on the initial nitrate level.

Garside (1991) showed that the shift-up phenomenon might be an artifact, when nitrate uptake rates are normalized to the particulate nitrogen content, because of a changing ratio of detrital material to live phytoplankton with time. Dickson and Wheeler (1995) suggested that the changes in PN-specific nitrate uptake rates may result from variations in phytoplankton biomass instead of changes in phytoplankton specific activity. Kudela and Dugdale (2000) also reported the disappearance of an apparent shift-up response of nitrate uptake during the winter months, which are characterized by high detrital particulate nitrogen levels. However, they observed a shift-up type physiological response regardless of the normalization procedure during upwelling periods, when phytoplankton contribute most of the particulate nitrogen.

Our data also suggest that we cannot neglect the artifact caused by the high percentage of detrital PN at the beginning of the experiment, although there was a slight increase of chlorophyll-*a* specific nitrate uptake rates in the samples with nitrate addition. In Experiment 2000-2, however, the acceleration of nitrate specific uptake rates in response to nitrate additions was less evident in the chlorophyll-*a* normalization than in the particulate nitrogen normalization (Fig.6.6). Dickson and Wheeler (1995) estimated the percentage of phytoplankton nitrogen in the PN pool from the regression of PN and chlorophyll-*a* concentrations. In this regression, the intercept indicates the PN concentration when the chlorophyll-*a* concentration is zero, which represents detrital PN. In Experiment 2000-2, the mean intercept of the nitrate treatments was about 2.01 μM, which is about 67.7 % of the initial PN value (ca. 2.97 μM) and indicates the importance of detrital PN at the beginning of experiment. In contrast, the mean intercept for the

nitrate treatments was about 0.80 μM in Experiment 2000-1, which was about 15.4% of the initial PN value (ca. 5.02 μM), suggesting that most of the PN consisted of live phytoplankton (Fig.6.10).

6.5. Ecological importance of this study

As discussed in the previous sections, our nutrient addition experiments confirmed that the growth of phytoplankton over the middle shelf of the southeastern Bering Sea was limited by the availability of nitrogen. Nitrogen limitation occurred after the spring bloom and continued throughout summer. Whitledge *et al.* (1986) showed that phytoplankton depleted surface nutrients during the spring bloom and further inputs of nutrients to the surface layer were hampered by the strong stratification and fronts. High nutrient concentrations occurred below the pycnocline in the middle shelf, where nitrate was supplied by cross-shelf transport of high nutrient slope water in the bottom layer (Whitledge *et al.* 1986; Stabeno *et al.* 2001), and ammonium was produced by the decomposition of phytoplankton and/or benthic processes (Whitledge *et al.* 1986).

Early studies showed that strong winds, associated with low-pressure systems, deepen the pycnocline and entrain the nitrate and ammonium rich water into the nitrate depleted surface euphotic layer (Sambrotto *et al.* 1986; Whitledge *et al.* 1986). This process can support continued primary production in late spring and summer and supported approximately 37% of annual new production over the middle domain of the southeastern Bering Sea shelf (Sambrotto *et al.* 1986). However, in that study there was no analysis of how phytoplankton responded to the supply of high nitrate and ammonium water via wind mixing. Our study suggests that the interactions between ammonium and

nitrate, such as ammonium preference or ammonium inhibition of nitrate uptake, may slow the utilization of nitrate and result in prolonged summer production. Also, there is probably more summer phytoplankton production than previously estimated, since that estimate only considered the supply of nitrate due to mixing (Sambrotto *et al.* 1986).

However, we have to be cautious about drawing conclusions from our experiments. In our experiments, very high nitrate and ammonium concentrations were added in order to examine the response of phytoplankton. The actual changes of nutrient concentration due to the wind mixing may not be as large. Whitledge *et al.* (1986) estimated that the net increase of nitrate concentration in the upper 40m of the water column would range from 1.25 μM to 1.5 μM, due to wind mixing if ambient nitrate concentrations below the pycnocline were between 10 and 15 μM. In 1997, nitrate concentration below the pycnocline decreased to less than 5 μM due to either decreased horizontal transport or biological utilization because of increased light penetration (Rho 2000; Stabeno *et al.* 2001; Stockwell *et al.* 2001). Thus, the experiments may not show the actual 'shift-up' of phytoplankton physiology that would be caused by wind mixing.

We can estimate the increase of ammonium concentration in the upper 40m due to wind mixing if the ambient ammonium concentration below the pycnocline ranged from 5 to 16 μM. The increase in ammonium may range from 0.6 to 1.5 μM, which might not be large enough to significantly influence the interaction between nitrate and ammonium as we observed from this study. However, it may increase the total production more than the previous estimates of the effect of wind mixing, which considered only nitrate supply into the surface layer (Sambrotto *et al.* 1986; Whitledge *et al.* 1986). As seen in chapter

3, the contribution of summer production to the total annual production ranged from 22.5 % to 27.3% over the southeastern Bering Sea shelf. When the large ammonium concentrations occurred in early spring of 1998, the interaction between ammonium and nitrate may have delayed the utilization of nitrate and increased the total production, although an increase of primary production was not observed in our production measurements. However, there were few production measurements during the spring of 1998, and the peak production period was not sampled.

6.6. Conclusion

Nutrient addition study suggests that nitrogen was limiting growth of phytoplankton after the spring phytoplankton bloom and continued throughout summer. Silicate was also controlling factor when diatoms were present water column. Nitrate uptake rates were severely inhibited when external ammonium concentrations were about 3- 7 μM. However, carbon uptake rates were not changed by different nitrogen source. Thus, this study suggests that the occurrence of high ammonium concentration in early spring of 1997 and 1998 may result in increase of total annual primary production. The contribution of summer primary production to total annual production over the middle shelf of the southeastern Bering Sea may be more important than previously estimated due to the simultaneous input of nitrate and ammonium by wind mixing event.

References

Bates, S. S. (1976). Effects of light and ammonium on nitrate uptake by two species of estuarine phytoplankton. Limnology and Oceanography **21**: 212-218.

Bienfang, P. K. (1975). Steady state analysis of nitrate-ammonium assimilation by phytoplankton. Limnology and Oceanography **20**: 402-411.

Butz, G. R. and W. A. Jackson (1977). A mechanism for nitrate transport and reduction. Phytochemistry **16**: 409-417.

Cochlan, W. P. and P. J. Harrison (1991). Inhibition of nitrate by ammonium and urea in the eucaryotic picoflagellate *Micromonas pusilla* (Butcher) Manton et Parke. Journal of Experimental Marine Biology and Ecology **153**: 143-152.

Collos, Y. and G. Slawyk (1980). Nitrogen uptake and assimilation by marine phytoplankton. Primary Productivity in the Sea. P. G. Falkowski (ed). New York, Plenum Press: 195-211.

Conway, H. L. (1977). Interactions of inorganic nitrogen in the uptake and assimilation by marine phytoplankton. Marine Biology **39**: 221-232.

DeManche, J. M., H. C. J. Curl, D. W. Lundy, and P. L. Donaghy (1979). The rapid response of the marine diatom *Skeletonema costatum* to changes in external and internal nutrient concentration. Marine Biology **53**: 323-333.

Dickson, M. L. and P. A. Wheeler (1995). Nitrate uptake rates in a coastal upwelling regime: A comparison of PN-specific, absolute, and Chl-*a*-specific rates. Limnology and Oceanography **40**: 533-543.

Dortch, Q. (1982). Effect of growth conditions on accumulation of internal nitrate, ammonium, amino acids, and protein in three marine diatoms. Journal of Experimental Marine Biology and Ecology **61**: 243-264.

Dortch, Q. (1990). The interaction between ammonium and nitrate uptake in phytoplankton. Marine Ecology Progress Series **61**: 183-201.

Dortch, Q. and S. I. Ahmed (1979). Nitrate reductase and glutamate dehydrogenase activities in *Skeletonema costatum* as measures of nitrogen assimilation rates. Journal of Plankton Research **1**: 169-186.

Dortch, Q., J. R. J. Clayton, S. S. Thoreson, and S. I. Ahmed (1982). Response of marine phytoplankton to nitrogen deficiency: decreased nitrate uptake vs. enhanced ammonium uptake. Marine Biology **70**: 13-19.

Dortch, Q. and H. L. Conway (1984). Interactions between nitrate and ammonium uptake: variation with growth rate, nitrogen source and species. Marine Biology **79**: 151-164.

Dugdale, R. C. and J. J. Goering (1967). Uptake of new and regenerated forms of nitrogen in primary productivity. Limnology and Oceanography **12**: 196-206.

Dugdale, R. C. (1976). Nutrient cycles. The Ecology of the Sea. D. H. Cushing and J. J. Walsh (eds.) Philadelphia, Oxford: Blackwell Scientific Publications: 141-172.

Eppley, R. W., J. L. Coatsworth, and L. Solorzano (1969). Studies of nitrate reductase in marine phytoplankton. Limnology and Oceanography **14**: 194-205.

Garside, C. (1991). Shift-up and the nitrate kinetics of phytoplankton in upwelling systems. Limnology and Oceanography **36**: 1239-1243.

Glibert, P. M., J. J. Lipschultz, J. J. McCarthy, and M. A. Altabet (1982). Isotope dilution models of uptake and remineralization of ammonium by uptake and remineralization of ammonium by marine plankton. Limnology and Oceanography **27:**639-650.

Goering, J. J. and R. L. Iverson (1981). Phytoplankton distribution on the southeastern Bering Sea shelf. The Eastern Bering Sea Shelf: Oceanography and Resources. Vol. 2, Hood, D. W. and J. A. Calder (eds.), Seattle, University of Washington Press. 933-945.

Hansell, D. A., T. E. Whitledge, and J. J. Goering (1993). Patterns of nitrate utilization and new production over the Bering -Chukchi shelf. Continental Shelf Research **13**: 601-627.

Holmes, R. W., P. M. Williams, and R. W. Eppley (1966). Red water in La Jolla Bay, 1964-1966. Limnology and Oceanography **12**: 503-512.

Horrigan, S. G. and J. J. McCarthy (1982). Phytoplankton uptake of ammonium and urea during growth on oxidized forms of nitrogen. Journal of Plankton Research **4**: 379-389.

Kudela, R. M. and R. C. Dugdale (2000). Nutrient regulation of phytoplankton productivity in Monterey Bay, California. Deep-Sea Research II **47**: 1023-1053.

Lessard, E. J., M. S. Foy, and J. R. Graff (2002). Summer phytoplankton and microzooplankton trophic dynamics on the SE Bering Sea shelf. Eos, Transactions, American Geophysical Union **83, Ocean Science Meeting Suppl. Abstract OS31D-70.**

MacIsaac, J. J., R. C. Dugdale, R. T. Barber, D. Blasco, and T. T. Packard (1985). Primary production cycle in an upwelling center. Deep-Sea Research **32**: 503-529.

McCarthy, J. J. (1980). Nitrogen. The physiological ecology of phytoplankton. I. Morris (ed.). Berkeley, Univ. California Press**:** 191-233.

McCarthy, J. J. (1981). The kinetics of nutrient utilization. Physiological Bases of Phytoplankton Ecology. T. Platt. Ottawa (ed), Department of Fisheries and Oceans. **Bulletin 210**.

Ohmori, M., K. Ohmori, and H. Strotmann (1977). Inhibition of nitrate uptake by ammonia in a blue-green alga, *Anabaena cylindrica*. Archives of Microbiology **114**: 225-229.

Parsons, T. R., Y. Maita, and C. M. Lalli (1984). A manual of chemical and biological methods for seawater analysis, Pergamon Press. 173 pp.

Rho, T. K. (2000). Carbon and nitrogen uptake dynamics during 1997 and 1998 anomalous conditions in the Bering Sea. M.S. Thesis, University of Alaska Fairbanks: 95pp.

Sambrotto, R. N., H. J. Niebauer, J. J. Goering, and R. L. Iverson (1986). Relationships among vertical mixing, nitrate uptake, and phytoplankton growth during the spring bloom in the southeast Bering Sea middle shelf. Continental Shelf Research **5**: 161-198.

Shoaf, W. T. and B. W. Lium (1976). Improved extraction of chlorophyll-*a* and -*b* from algae using dimethyl sulfoxide. Limnology and Oceanography **21**: 926-928.

Slawyk, G., Y. Collos, and J. C. Auclair (1977). The use of the ^{13}C and ^{15}N isotopes for the simultaneous measurement of carbon and nitrogen turnover rates in marine phytoplankton. Limnology and Oceanography **22**: 925-932.

Stabeno, P. J., N. A. Bond, N. B. Kachel, S. A. Salo, and J. D. Schumacher (2001). On the temporal variability of the physical environment over the south-eastern Bering Sea. Fisheries Oceanography **10**: 81-98.

Stockwell, D. A., T. E. Whitledge, S. I. Zeeman, K. O. Coyle, J. M. Napp, R. D. Brodeur, A. I. Pinchuk, and G. L. Hunt, Jr. (2001). Anomalous conditions in the south-eastern Bering Sea, 1997: nutrients, phytoplankton and zooplankton. Fisheries Oceanography **10**: 99-116.

Syrett, P. J. (1981). Nitrogen metabolism of microalgae. Canadian Bulletin Fisheries Aquatic Science **210**: 182-210.

Syrett, P. J. and J. W. Leftley (1976). Nitrate and urea assimilation by algae. Perspectives in Experimental Biology 2. Botany. N. Sunderland (ed). Oxford, Pergamon Press: 221-234.

Thompson, P. A., M. E. Levasseur, and P. J. Harrison (1989). Light-limited growth on ammonium vs. nitrate: What is the advantage for marine phytoplankton? Limnology and Oceanography **34**: 1014-1024.

Wheeler, P. A. and S. A. Kokkinakis (1990). Ammonium recycling limits nitrate use in the oceanic subarctic Pacific. Limnology and Oceanography **35**: 1267-1278.

Whitledge, T. E., W. S. Reeburgh, and J. J. Walsh (1986). Seasonal inorganic nitrogen distributions and dynamics in the southeastern Bering Sea. Continental Shelf Research **5**: 109-132.

Whitledge, T. E., D. M. Veidt, S. C. Malloy, C. J. Patton, and C. D. Wirick (1981). Automated nutrient analyses in seawater, Brookhaven National Laboratory. 216 pp.

Wilkerson, F. P. and R. C. Dugdale (1987). The use of large shipboard barrels and drifters to study the effects of coastal upwelling on phytoplankton dynamics. Limnology and Oceanography **32**: 368-382.

Yin, K., P. J. Harrison, and Q. Dortch (1998). Lack of ammonium inhibition of nitrate uptake for a diatom grown under low light conditions. Journal of Experimental Marine Biology and Ecology **228**: 151-165.

Zevenboom, W. and L. R. Mur (1981). Simultaneous short-term uptake of nitrate and ammonium by *Oscillatoria agardhii* grown in nitrate-or light-limited continuous culture. Journal of Genetic Microbiology **126**:355-363.

Zimmerman, R. C., J. N. Kremer, and R. C. Dugdale (1987). Acceleration of nutrient uptake by phytoplankton in a coastal upwelling ecosystem: A modeling analysis. Limnology and Oceanography **32**: 359-367.

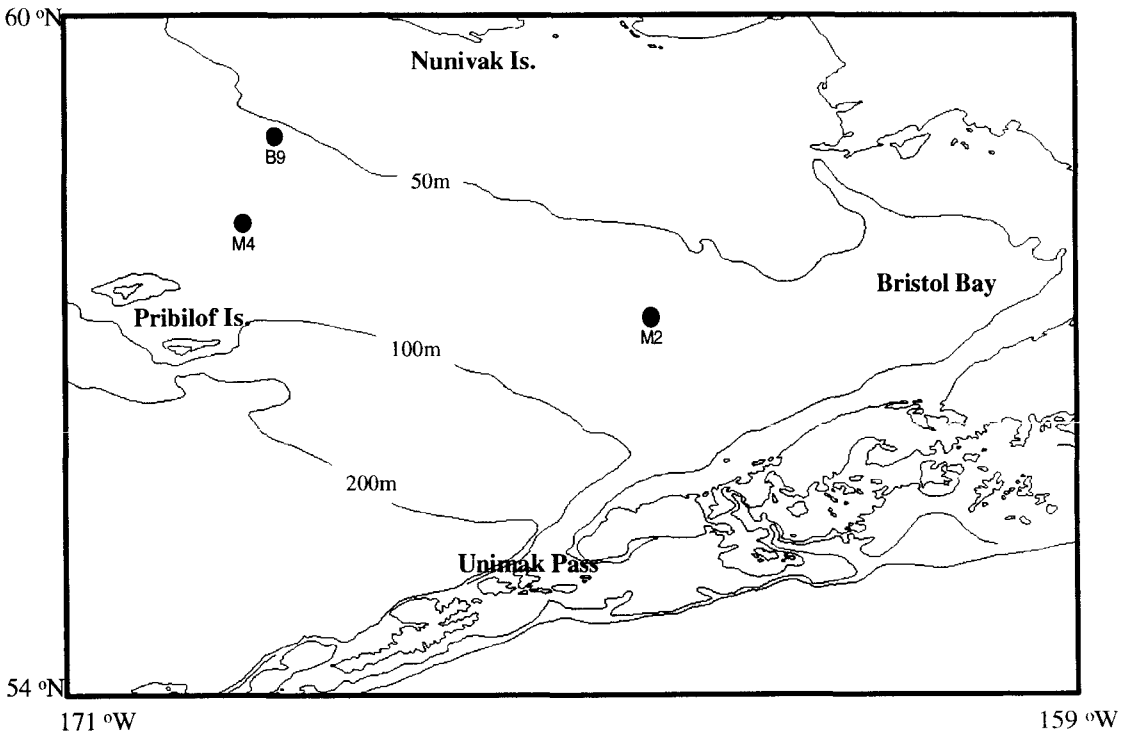

Fig.6.1. Station locations of the nutrient addition study over the southeastern Bering Sea shelf during the summers of 2000 and 2001.

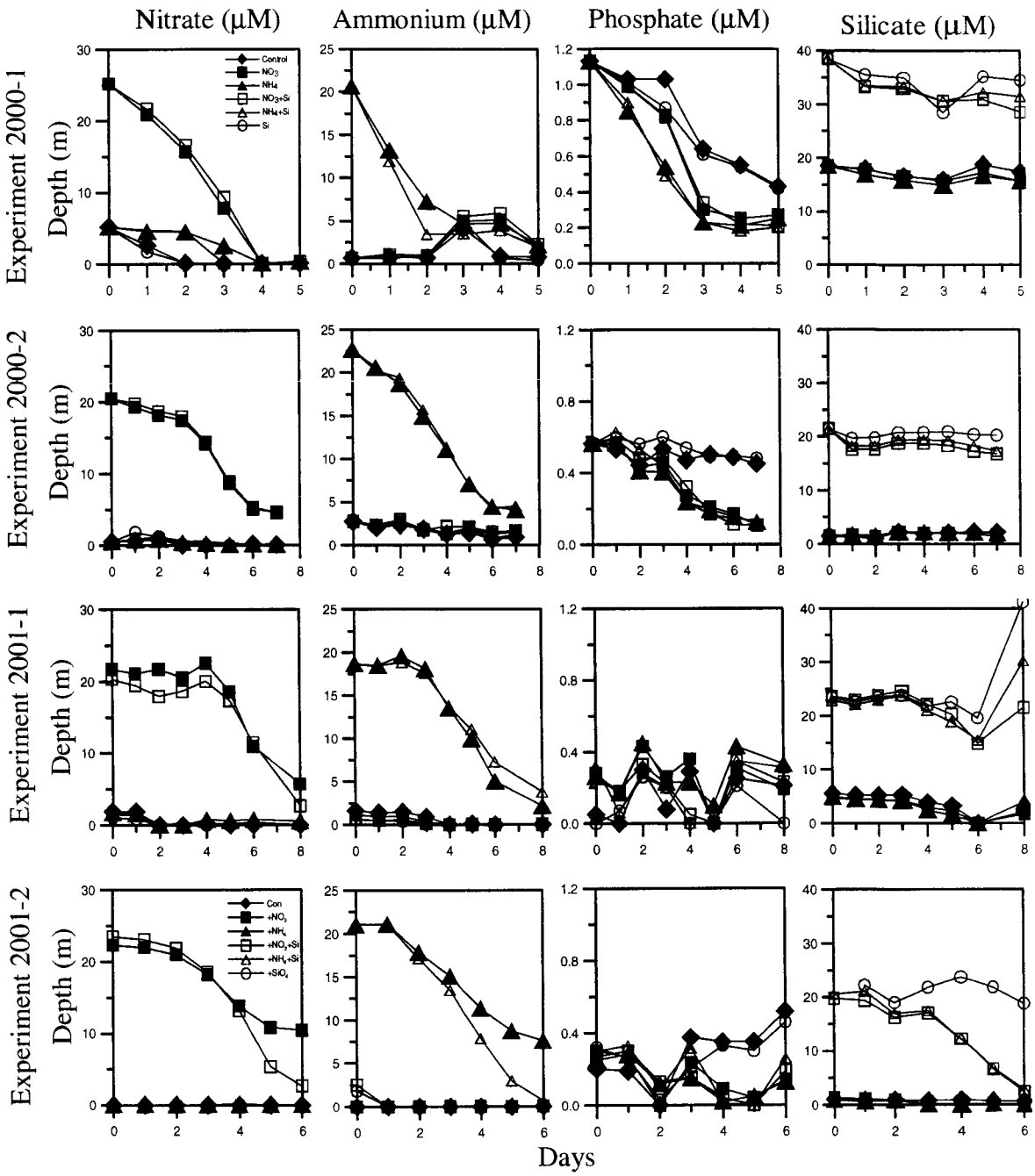

Fig.6.2. Changes of nutrient concentrations with time during the nutrient addition study. In here, Con indicates control, $+NO_3$ indicates nitrate addition, $+NH_4$ indicates ammonium addition, $+NO_3+SiO_2$ indicates nitrate and silicate additions, $+NH_4+SiO_2$ indicates ammonium and silicate addition, and $+SiO_2$ indicates silicate addition.

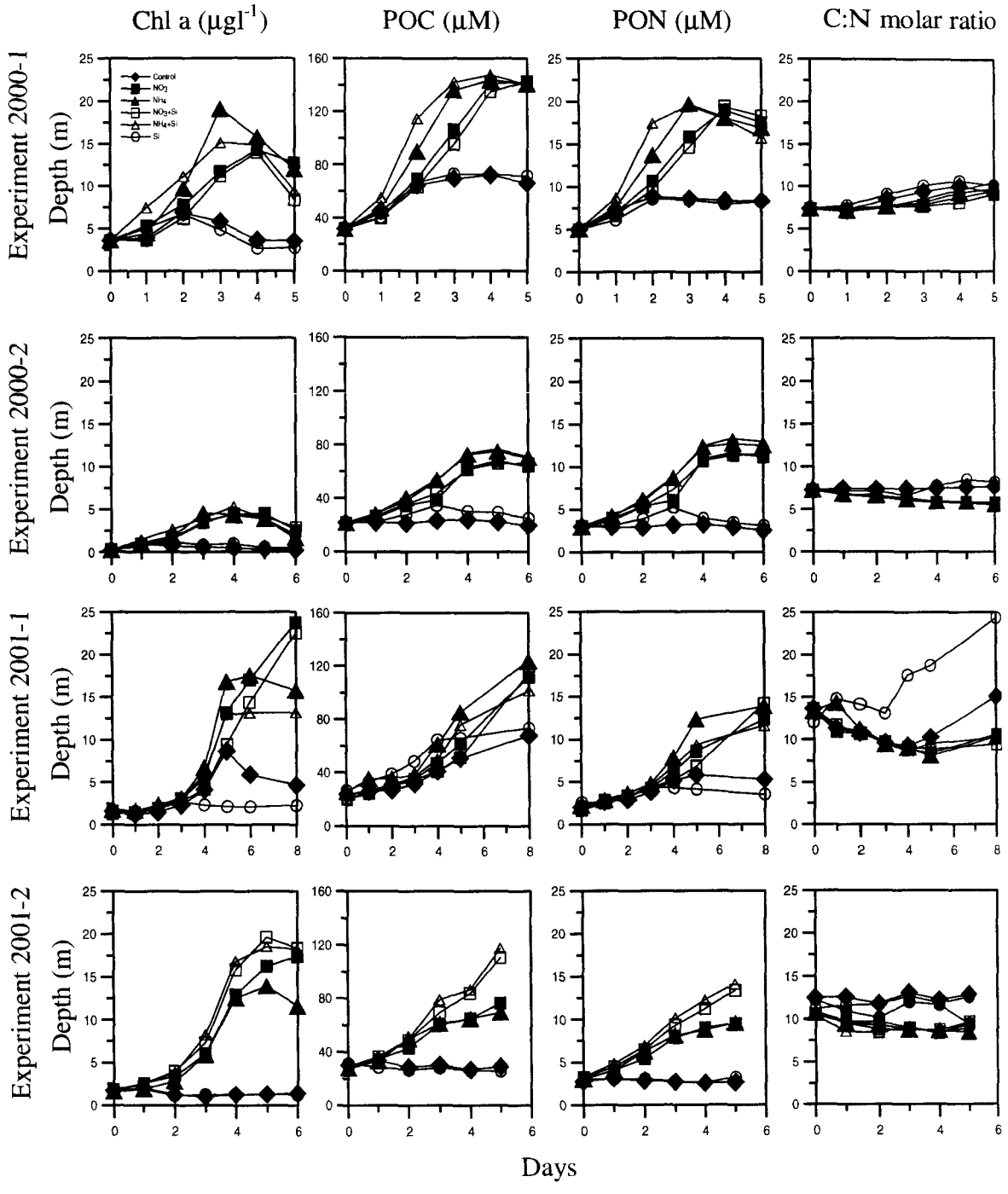

Fig.6.3. Changes of chlorophyll-*a*, POC, PON, and C:N molar ratio with time during the nutrient addition study. In here, Con indicates control, $+NO_3$ indicates nitrate addition, $+NH_4$ indicates ammonium addition, $+NO_3+SiO_2$ indicates nitrate and silicate additions, $+NH_4+SiO_2$ indicates ammonium and silicate addition, and $+SiO_2$ indicates silicate addition.

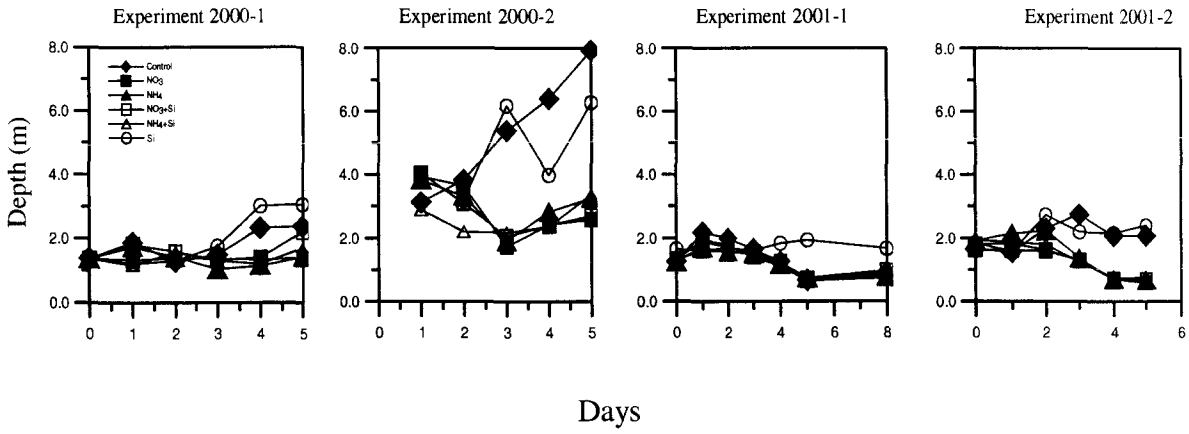

Fig.6.4. Changes of PN:Chl-*a* ratio (mg at N: mg chl *a*) with time during the nutrient addition study. In here, Con indicates control, $+NO_3$ indicates nitrate addition, $+NH_4$ indicates ammonium addition, $+NO_3+SiO_2$ indicates nitrate and silicate additions, $+NH_4+SiO_2$ indicates ammonium and silicate addition, and $+SiO_2$ indicates silicate addition.

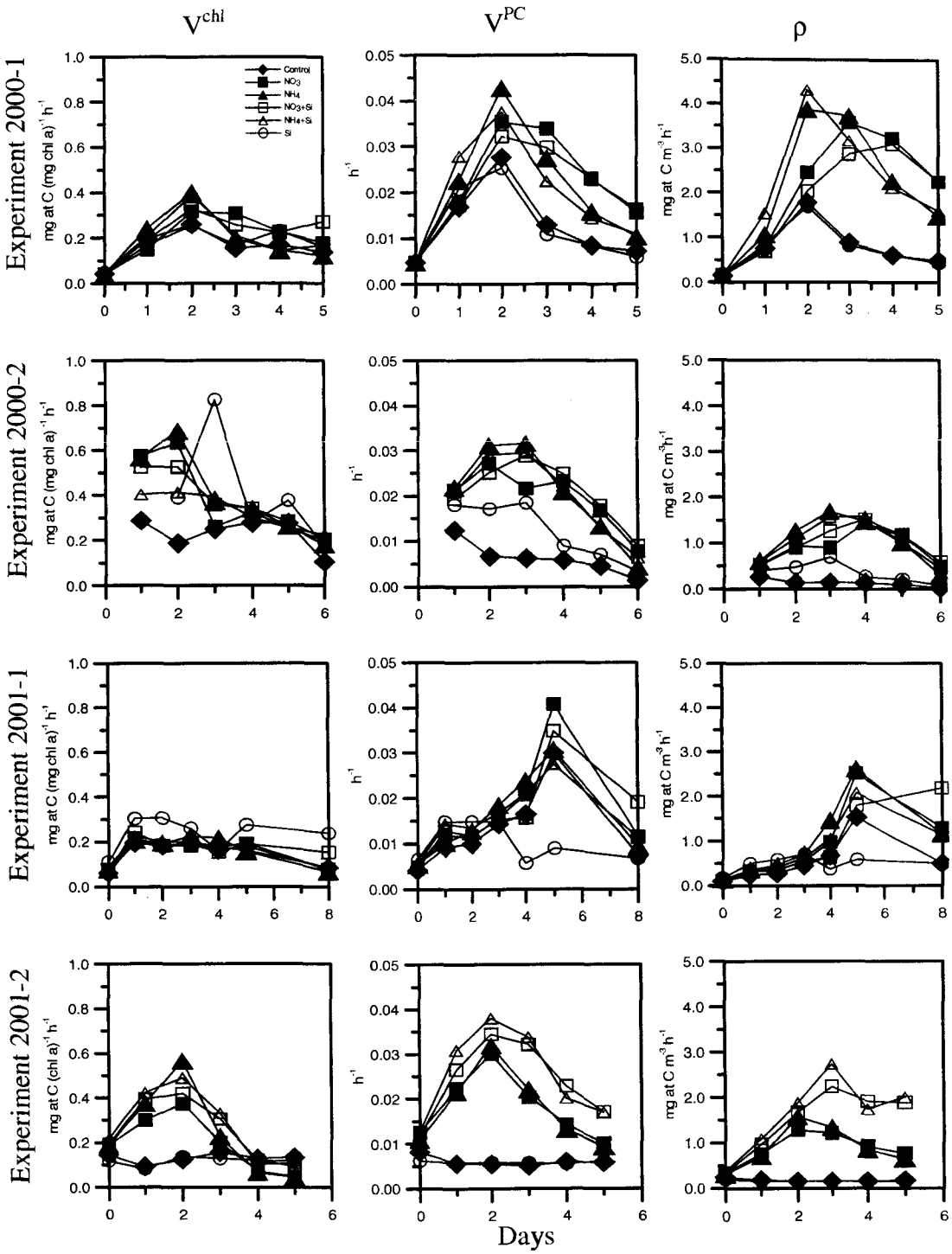

Fig.6.5. Carbon uptake rates [chlorophyll a specific (V^{chl}), particulate carbon specific (V^{PC}), and absolute (ρ) uptake rates] with time during the nutrient addition study. In here, Con indicates control, $+NO_3$ indicates nitrate addition, $+NH_4$ indicates ammonium addition, $+NO_3+SiO_2$ indicates nitrate and silicate additions, $+NH_4+SiO_2$ indicates ammonium and silicate addition, and $+SiO_2$ indicates

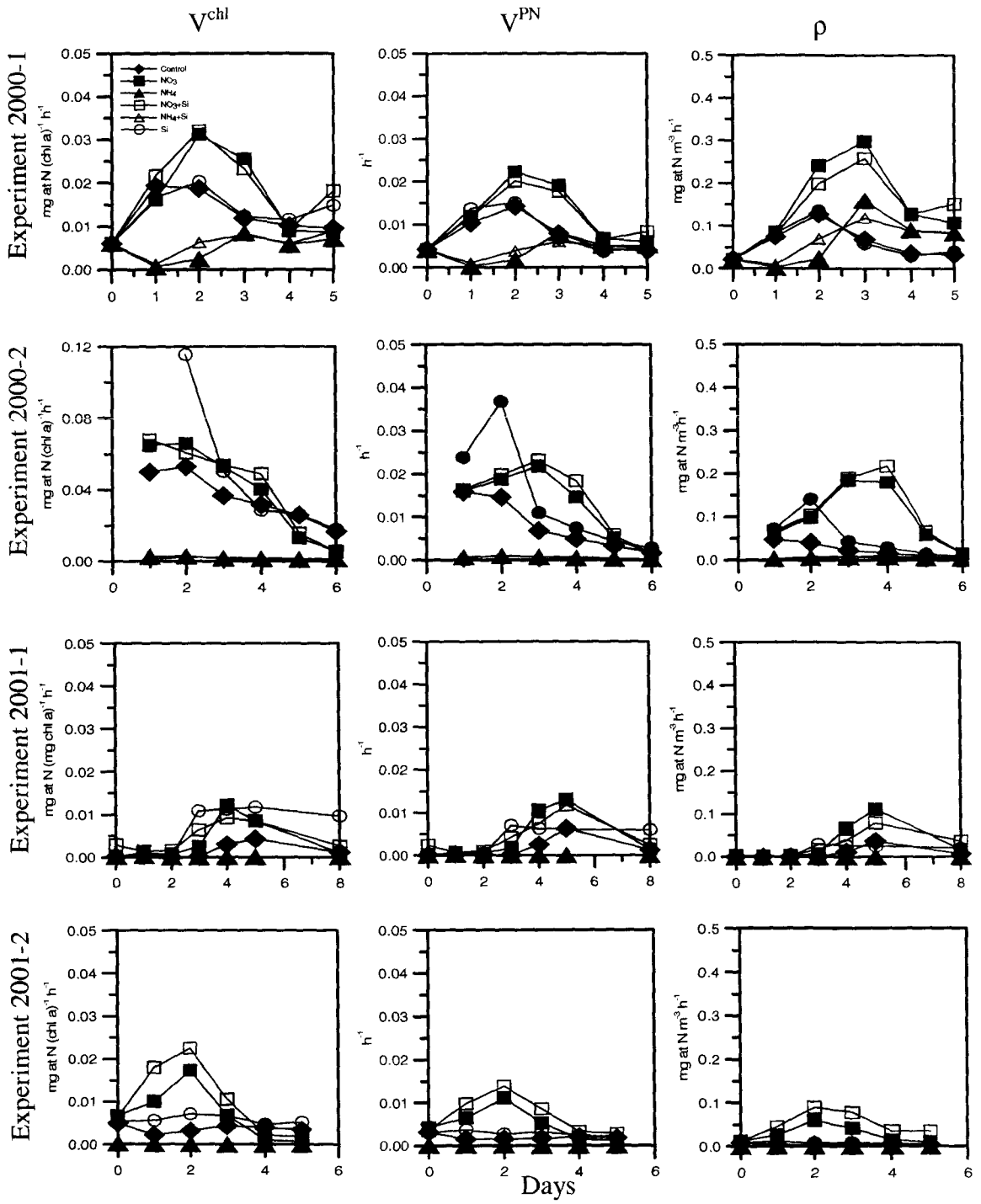

Fig.6.6. Nitrate uptake rates [chlorophyll a specific (V^{chl}), particulate nitrogen specific (V^{PN}), and absolute (ρ) uptake rates] with time during the nutrient addition study. In here, Con indicates control, $+NO_3$ indicates nitrate addition, $+NH_4$ indicates ammonium addition, $+NO_3+SiO_2$ indicates nitrate and silicate additions, $+NH_4+SiO_2$ indicates ammonium and silicate addition, and $+SiO_2$ indicates silicate addition.

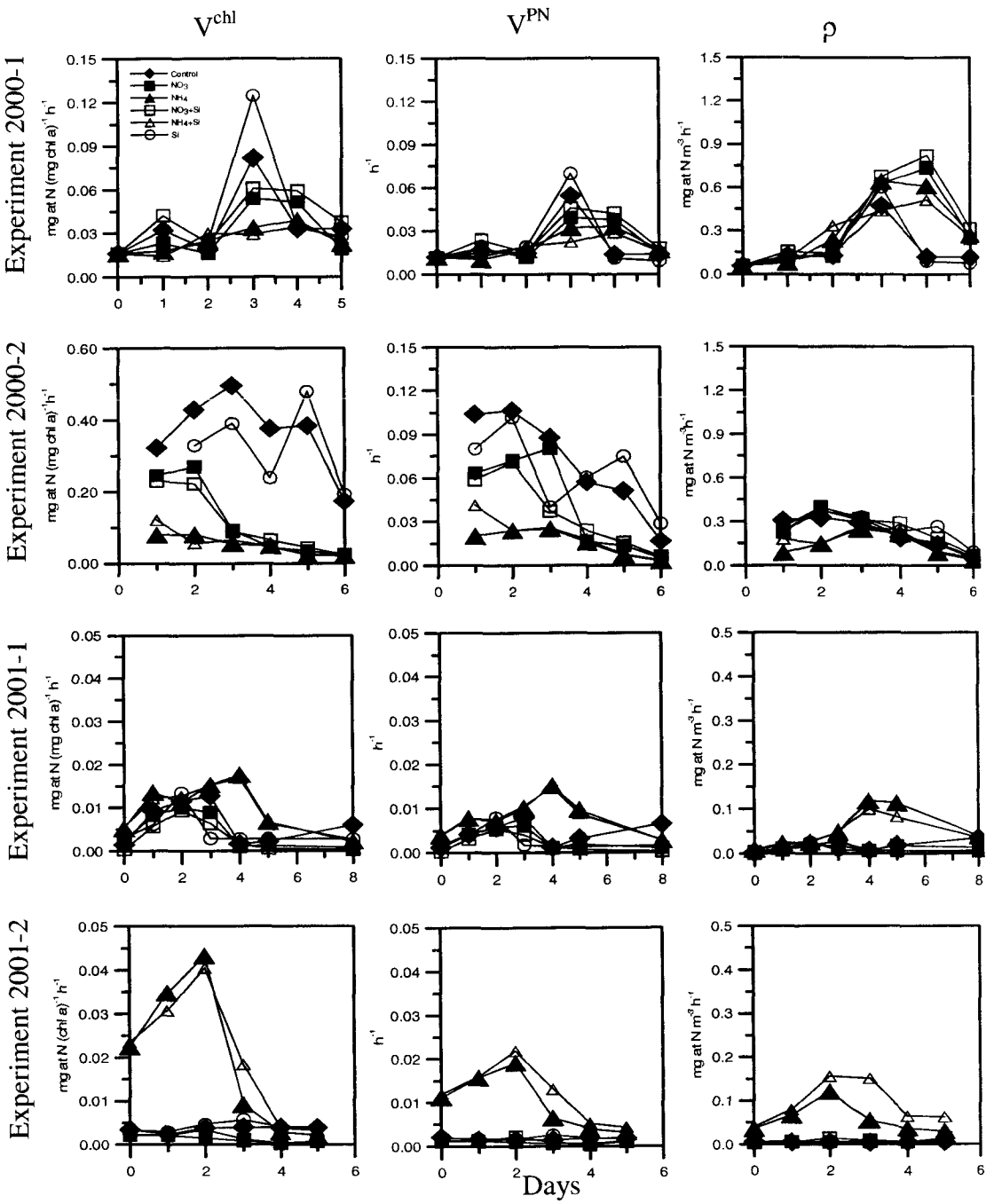

Fig.6.7. Ammonium uptake rates [chlorophyll a specific (V^{chl}), particulate nitrogen specific (V^{PN}), and absolute (ρ) uptake rates] with time during the nutrient addition study. In here, Con indicates control, $+NO_3$ indicates nitrate addition, $+NH_4$ indicates ammonium addition, $+NO_3+SiO_2$ indicates nitrate and silicate additions, $+NH_4+SiO_2$ indicates ammonium and silicate addition, and $+SiO_2$ indicates silicate addition.

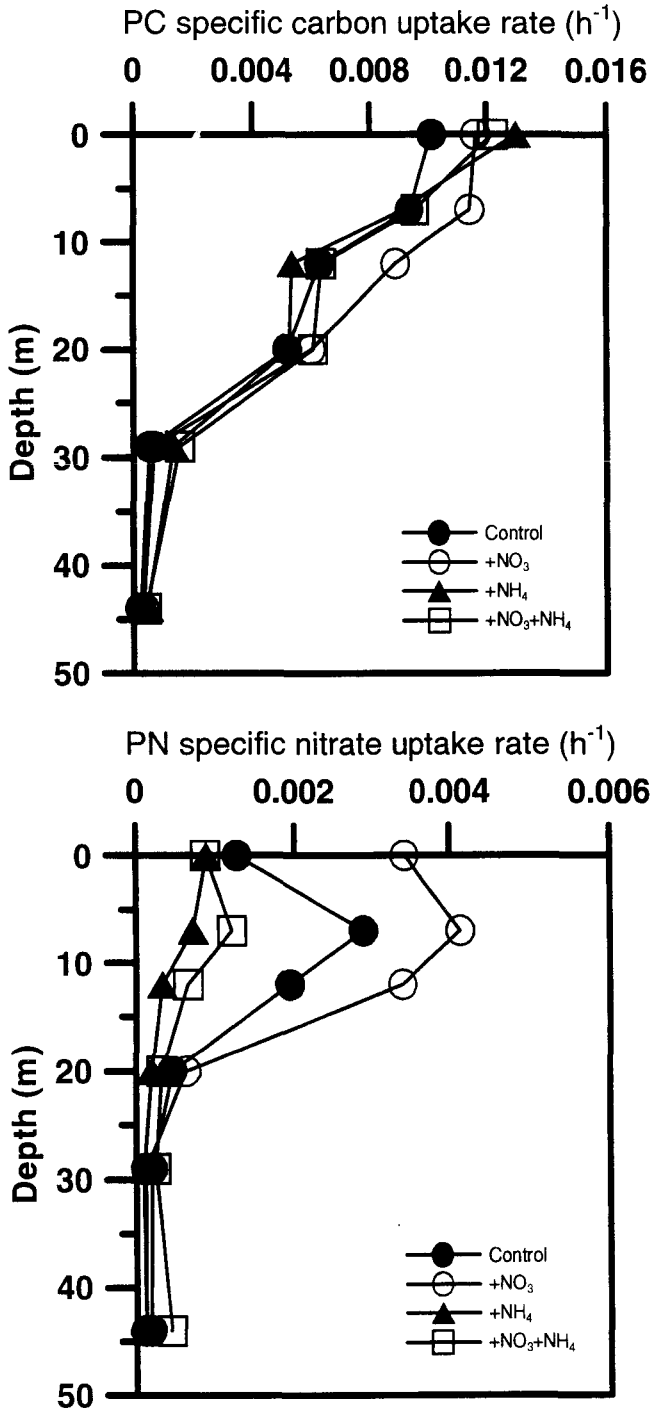

Fig.6.8. PC specific carbon uptake rates (upper) and PN specific nitrate uptake rates (lower) with different nutrient treatments at M2 during the summer of 2000. In here, control indicates no nitrogen addition, $+NO_3$ indicates nitrate addition, $+NH_4$ indicates ammonium addition, and $+NO_3+NH_4$ indicates nitrate and ammonium additions.

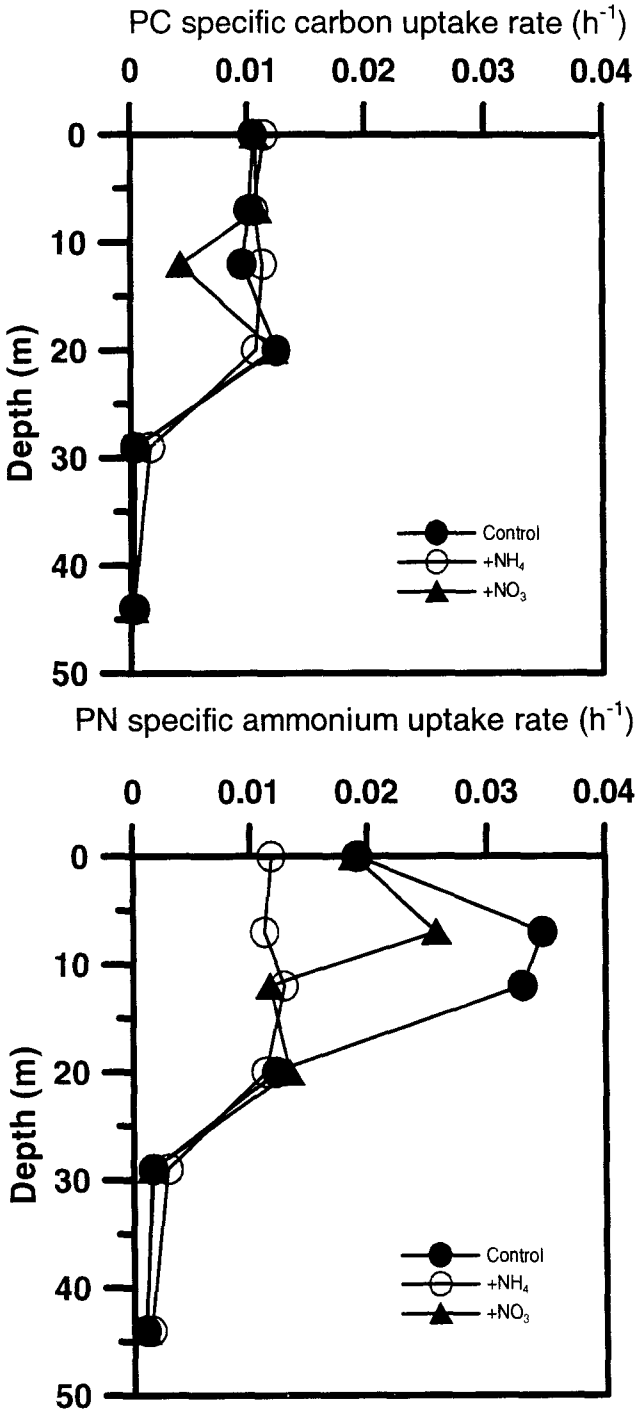

Fig.6.9. PC specific carbon uptake rates (upper) and PN specific ammonium uptake rates (lower) with different nutrient addition at M4 during the summer of 2000. In here, control indicates no nitrogen addition, and $+NH_4$ indicates ammonium addition, and $+NO_3$ indicates nitrate addition

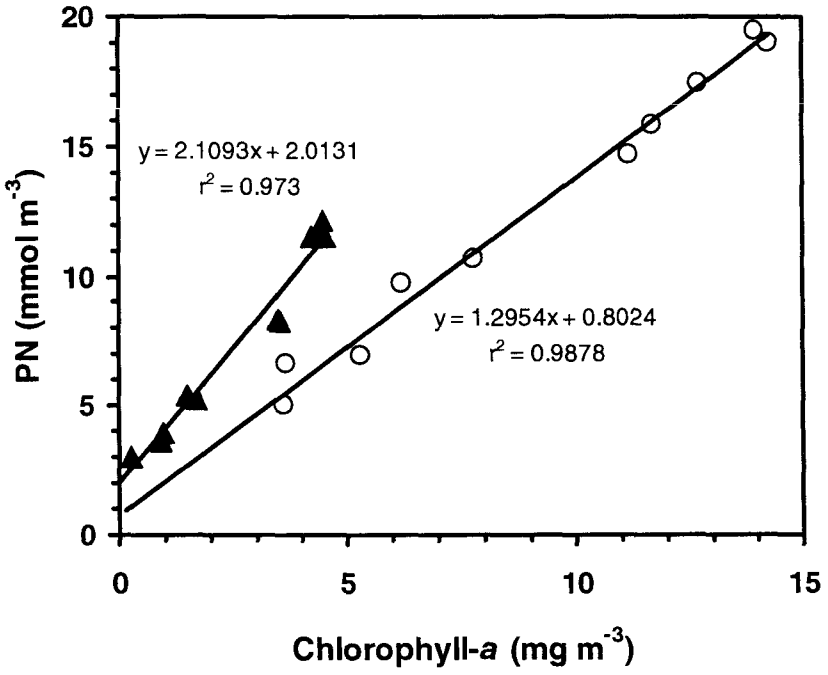

Fig.6.10. Regression of PN and Chl-*a* in the $+NO_3^-$ and $+NO_3^-+SiO_2$ treatments of Experiment 2000-1 (open circles) and Experiment 2000-2 (closed triangles).

Chapter 7. Summary and Recommendation for Future Study

7.1. Summary

Because of the varying and unpredictable timing of the spring bloom and the fixed cruise schedules of ships, we were unable to obtain enough measurements to estimate accurately the spring primary production over the southeastern Bering Sea shelf during the distinctively different physical conditions of 1997, 1998, and 1999. Salinity, temperature, and nutrient concentrations showed strong interannual variations in response to variations of sea ice dynamics and wind mixing, which in turn are closely related to the changes in large-scale climate conditions. Carbon and nitrogen uptake rates responded to the changes in physical conditions. The occurrence of high ammonium concentrations in early spring of 1997 and 1998 over the middle shelf had not been observed previously, and may be related to warm temperatures that increased zooplankton populations or bacterial remineralization of organic material. Alternatively, high ammonium could have resulted from the direct or indirect influence of melting sea ice. Whatever the cause, it is necessary to consider the interaction between ammonium and nitrate in future ecosystem models of this region.

Our study showed that annual primary production was similar over the inner, the middle, and the outer shelves, and the shelf break. It should be noted that our analysis suggested that primary production over the shelf break regions of the southeastern Bering Sea was not much higher than that of other regions. In the shelf break region, primary production showed seasonal cycles with high production in May and June, but the maximum production rates were lower than those of the middle and outer shelf. There

were also interannual variations in the timing of the development of the phytoplankton bloom across the shelf, which were closely related to the strength of upwelling and the slope of the front at the shelf break region. There were latitudinal variations of primary production. High production occurred early in the southern part of the shelf and occurred later in the northern part. The mean value of primary production from 1997 to 2000 was only about 36% of that measured during the PROBES study, but that might have resulted from the incomplete seasonal and spatial coverage of measurements during 1997-2000, which did not sampled the spring bloom. In general, spring production constituted 41-55% of the total annual production over the shelf region, and summer and fall production constituted 41.6-59.0% of the total annual production.

Shipboard incubations of surface water from inside and outside of the shelf break showed that phytoplankton did not utilize nutrients completely in the incubation bottles within 5 days. This is very similar to results from regions where the availability of iron limits the growth of phytoplankton and the complete utilization of nutrients (Price *et al.* 1994; Boyd *et al.* 1996). However, unlike the iron-limited regions, biomass gradually increased toward day 5. This suggested that the availability of iron did not limit the growth of phytoplankton, but rather other processes such as ammonium inhibition or microzooplankton grazing were responsible for the incomplete utilization of nitrate in the incubation bottle. Our iron addition experiments confirmed that the growth of phytoplankton was not changed by the addition of iron in either the middle shelf or the shelf break experiments. However, the carbon and nitrate uptake rates were enhanced by the addition of iron in the shelf break experiment, which suggested that phytoplankton

growth in the shelf break region may be slightly inhibited by low iron conditions, very similar to those observed in the California coastal upwelling region (Hutchins *et al.* 1998). The offshore transport of middle shelf water at mid-depth may supply regenerated iron into the shelf break region, as suggested by the distribution of the ammonium concentration and the 3° C isotherm at mid-depth over the outer shelf.

Our nutrient addition study showed that, during summer, nitrogen was the limiting nutrient for the growth of phytoplankton, but silicate was a controlling factor when diatoms were present in the water column. Nutrient utilization and specific nitrate uptake rates suggested that high external ammonium concentrations suppressed the nitrate uptake rates. The inhibition of nitrate uptake rates by ammonium was most obvious in the small bottle nitrate uptake measurements, which showed that nitrate uptake rates decreased to 43% of the control with ammonium addition. The decrease of nitrate uptake rates was more dramatic in response to the combined addition of nitrate and ammonium, compared with the addition of nitrate alone. The integrated nitrate uptake rate after the combined addition of nitrate and ammonium was ca. 26% of that in the nitrate addition bottle. However, there was no apparent difference in carbon uptake rates between bottles with nitrate additions and those with ammonium additions. Thus, the simultaneous input of ammonium and nitrate by wind mixing events over the middle shelf during summer may be more important than previously estimated, in terms of total production, because the previous estimates did not include effects of the supply of ammonium into the surface euphotic layer.

Nitrate uptake rates showed a 'shift-up' response to the favorable light and high nitrate concentrations in our experiments, which suggested that phytoplankton growth rates may increase in response to the supply of nutrients into the surface euphotic layer by wind mixing in the middle shelf during summer. However, our results also showed that the apparent shift-up in PON specific nitrate uptake rates disappeared when nitrate uptake rates were normalized to chlorophyll concentration.

7.2. Recommendations for future study

This study showed that there were large temporal and spatial variations in the development of the spring phytoplankton bloom. The fate of primary production was closely related to changes in the strength and the slope of the shelf break front, both of which could be connected to variations in climate. However, the spring bloom, which supplies nearly half of the annual production and so is key to understanding productivity variation was not sampled during 1997-2000. Thus, to better understand changes of the ecosystem dynamics over the southeastern Bering Sea, it is necessary to increase the temporal and spatial resolution of the primary production measurements, especially, in the shelf break and over the inner shelf. The improved sampling is especially important in the shelf break region to better understand the very productive higher trophic levels.

Another limitation of this dissertation research is that our nutrient addition study was not a completely realistic simulation of the nutrient supply into the nutrient depleted surface euphotic layer by wind mixing, because we added too much nutrient. Thus, we need more experiments with low nutrient additions to simulate a more realistic response

to wind-driven nutrient supply during summer. This could provide very valuable information for ecosystem and productivity models.

References

Boyd, P. W., D. L. Muggli, D. E. Varela, R. H. Goldblatt, R. Chretien, K. J. Orians, and P. J. Harrison (1996). *In vitro* iron enrichment experiments in the NE subarctic Pacific. Marine Ecology Progress Series **136**: 179-193

Hutchins, D. A., G. R. DiTullio, Y. Zhang, and K. W. Bruland (1998). An iron limitation mosaic in the California upwelling regime. Limnology and Oceanography **43**: 1037-1054.

Price, N. M., B. A. Ahner, and M. M. Morel (1994). The equatorial Pacific Ocean: Grazer-controlled phytoplankton populations in an iron-limited ecosystem. Limnology and Oceanography **39**: 520-534.